Swedish University of Agricultural Sciences
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Epoxidised linseed oil as hydrophobic substance for wood protection
- technology of treatment and properties of modified wood

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Master Thesis
No 126 2013

ISSN 1654-1367

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Keywords: Dimensional stability, epoxidised linseed oil, FT-IR spectroscopy, impregnation, leaching, linseed oil, mechanical properties, modified wood, Scots pine sapwood, two-step process

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Master Thesis, 30 ECTS credit *Advanced level in Forest Management (EX0660)*

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Sammanfattning

Allmänhetens oro över utsläpp av giftiga ämnen ifrån träbaserade produkter driver lagstiftning och därmed industrier att hitta och använda mer hållbara lösningar för behandling av trä. Växtoljor är bra alternativ för att behandla trä då de minimerar eller helt eliminerar miljöeffekterna. Trämodifiering med epoxiderad linolja (ELO) och ättiksyra som katalysator har visat sig vara en lämplig metod för att impregnera och skydda trä.

Dock är ELO/ättiksyreblandningen praktiskt svår att hantera på grund av en snabb polymerisering av dessa ingredienser vilket begränsar dess praktiska tillämpning. På grund av den begränsningen har därför denna studie utformats för att utvärdera en alternativ metod bestående av en 2-stegs impregneringsprocess vilken undanröjer noterade problem. Flera behandlingsalternativ baserat på denna nya föreslagna metod har testats på tallsplintved. Resultaten utvärderades genom bestämning av dimensionsstabilitet, samt hydrofoba och mekaniska egenskaperna hos det behandlade träet.

Den föreslagna metoden uppvisar mycket god dimensionsstabilitet hos behandlat material, den uppmätta ”anti-swelling efficiency” (ASE, ”anti-svullnads effektivitet”) låg i intervallet 40-55%. Referensprover av termiskt modifierat trä visade endast 40% ASE. ELO-addition till trä studerades med FT-IR-spektroskopi. Modifieringen påverkade brotthållfastheten negativt emedan elasticitetsmodul, hårdhet och tryckhållfasthet hos behandlat trä var nästan oförändrad. Slutsatsen är att den föreslagna tvåstegsprocessen verkar vara en möjligt och praktisk genomförbar lösning för ELO-behandling av trä.

***Nyckelord**: epoxiderad linolja, tallsplintved, dimensionsstabilitet, FT-IR-spektroskopi, linolja, trämodifiering, 2-stegs impregneringsprocess, mekaniska egenskaper*

Abstract

Public concern about the release of toxic compounds from wood-based products drives legislation towards enforcing industries to find and use more sustainable solutions for wood treatment. Plant oils are good alternatives to treat wood, minimizing or even neutralizing the impact on the environment. Wood modification with epoxidised linseed oil (ELO) and acetic acid as catalyst has proven a suitable method to impregnate and protect wood. However, the mixture presents a serious inconvenience because of the quick polymerization of the ingredients that limits its practical application. Therefore, this study was designed to evaluate an alternative method using a two-step process which bypassed the problem above. Several treatment options using this method onto Scots pine sapwood were tested. The results were evaluated by determining the dimensional stability, hydrophobic and mechanical properties of the treated wood.

The studied treatments provided very good dimensional stability of the material, the measured anti-swelling efficiency (ASE) was in the range 40-57%. Reference samples of thermally modified wood showed only 40% ASE. The grafting of ELO to the wood polymeric constituents was studied using FT-IR spectroscopy. The modification influenced negatively the modulus of rupture, while the modulus of elasticity, hardness and compression strength of the material was almost unchanged. It can be concluded that the two-step process method seems a possible and feasible practical solution for ELO treatment of wood.

Keywords: *Linseed oil, epoxidised linseed oil, Scots pine sapwood, impregnation, two-steps process, modified wood, dimensional stability, leaching, mechanical properties, FT-IR*

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List of abbreviations

AA	Acetic acid	MOR	Modulus of rupture
AC	Acetylation	NA	Not applicable
ASE	Anti-swelling efficiency	OD	Oven-dried/oven-drying
BA	Boric acid	R	Radial
C	Concentration	R^2	Regression coefficient
CCA	Chromated copper arsenate	RH	Relative humidity
ELO	Epoxidised linseed oil	SD	Standard deviation
FT-IR	Fourier transform infrared spectroscopy	T	Tangential
HB	Hardness (Brinell)	TM	Thermal modification
L	Longitudinal	UV	Ultraviolet
LF	Leached formulation	V	Volume
LO	Linseed oil	W	Weight
MC	Moisture content (on dry basis)	WPG	Weight percentage gain
Mix.	Mixture	WS	Water-soaked/water-soaking
MOE	Modulus of elasticity	WSOD	Water-soaking and oven-drying

1 Introduction

Wood is an irreplaceable material used by mankind over the centuries that still today continues to have a great range of applications. Wood characteristics comprise advantages and drawbacks depending on the intended use. Processing and utilization of timber have some apparent drawbacks when compared to other materials because wood is a biological material which entails two important aspects: 1) wood is composed by organic tissue, which can be degraded by environmental conditions or microorganisms, insects and marine borers, and 2) wood has great variability in its properties, varying among species, stands, trees and even within different positions of the same tree. The variations (heterogeneity) cause difficulties in the manufacturing of wood-based products as well as for studying the material itself.

1.1 Wood degradation

Wood degradation by insects and fungi requires certain availability of oxygen, favorable temperature, moisture and nutrients (Eaton and Hale 1993). Limitation in one or more of these factors can lead to some degree of protection. Among the factors above, preventing wood from reaching certain moisture content (MC) is the easiest means to hinder microorganisms attack and degradation of wood. According to Schmidt (1994), cited in Sailer and Etten (2004), typical wood degrading fungi need a minimum MC between 17% (*e.g.* the brown rot fungus *Serpula lacrymans*) to 25% (*e.g.* the white rot fungus *Coriolus versicolor*) to begin wood colonization.

When wood is exposed to some external abiotic factors, physical and chemical degradation occur. This process is known as weathering. Wood is affected by sunlight (UV and visible light), moisture (snow, rain, dew and water vapour), heat (modifying reactions rates) and other factors (*e.g.* acid rain).

When used outdoors, wood-based products face significantly higher degree of degradation than those exposed indoors. A wood property which becomes greatly affected by these factors is the wood dimensional stability. Both moisture content and bio-degradability have a direct impact on wood dimensions.

1.2 Wood modification and protection

Modification is intended to change wood properties in such a way that a pre-selected improvement of the material's performance is permanently ensured during the service life of the product. Wood can be modified to various degrees; however, a basic differentiation can be made: 1) when modification achieves a change in the properties without altering the chemistry of the material; and 2) when modification alters the chemical nature of the material and thus, the properties are also changed. According to Hill (2006), "*chemical modification of wood is defined as the reaction of a chemical reagent with the wood polymeric constituents, resulting in the formation of a covalent bond between the reagent and the wood substrate"*.

Wood protection against biological attack is the most important aspect targeted by wood modification. The use of certain chemicals such as chromated copper arsenate (CCA) or creosote for wood protection has proven to be very effective against biological attack. However, these chemicals are harmful to humans and the environment. The release of toxic substances, leaching during service life and/or at disposal of the waste-wood, causes negative environmental impacts that have increasingly contributed to public concerns. Legislation changes have been constantly pressing the industry towards production of more

"environmentally-friendly" products and thus, the research and development of technologies using non-toxic ingredients for wood protection have continuously increased.

1.3 Plant oils

Plant oils are one of the natural alternatives to treat and protect wood. The oils have commonly been used for enhancing the appearance or extending the service life of wood items for centuries. Oils can be obtained from various parts of plants in a cost-effective manner. Tall and pyrolysis oils are two examples of plant oils that are extracted in a special way, *i.e.* by the kraft process of wood pulp manufacture when pulping mainly coniferous wood and anaerobic heating at 400-500°C respectively.

The vast majority of plant oils possess no fungicidal properties and are used for wood protection as "water repellent" substances (Panov *et al.* 2010). This demands very high retention of oil impregnated into the wood, often more than 400 kg/m^3, which does not make the use of plant oils economically viable. The second practical problem related to use of plant oils is their leaching or so-called "exudation" after impregnation since no chemical bonding exists between the oil and the main wood constituents.

The above outlines the main directions of current on-going research on plant oils for wood protection namely, decreasing the amount of oil needed, immobilization of oil in the wood cell wall by in-situ polymerization and encapsulation of fungicides with low environmental impact in the oil, for instance boron compounds.

Few oils possess some fungicidal properties; tall and pyrolysis oils are good examples of such oils. Paajanen and Ritschkoff (2002) studied three oils namely, tall, rapeseed and linseed oil as well as wood samples treated with the same oils for decay on sterilized malt agar inoculated with the fungi *Coniophora puteana*, *Poria placenta*, and *Coriolus versicolor.* The authors did a soil box test according to ENV 807 with tall oil treated samples against soft rot fungi. The conclusions were that tall oil had the best effect, especially on soft rot fungi, though none of the oils seemed to have a toxic influence on the test fungi (Paajanen and Ritschkoff 2002).

In another investigation (Alfredson *et al.* 2004), four refined tall oils with different contents of free fatty acids and free resin acids were first diluted with isopropanol to 25% tall oil content and then tested in a filter paper assay against *Postia placenta* and *Coriolus versicolor.* For this assay, 1 ml of the solution was pipetted onto filter paper and dried in a petri dish. Afterwards, a thin layer of 4% malt extract-agar was added on top of the paper and the fungi were added. While all tall oils were more efficient against *C. versicolor* than against *P. placenta*, there were differences between the inhibition capacities of the four oils; the efficacy against fungi increased with higher content of free resin acids in the tall oils. However, the following mini-block-assay with the same oils did not show a clear relation between the content of resin acids and effectiveness against fungi, though all of the refined tall oils were more efficient against *C. puteana* than against *P. placenta*. Two refined tall oils inhibited a mean mass loss higher than 10%.

Kartal *et al.* (2006) reported cassia oil and wood tar oil treatments from sugi wood (*Cryptomeria japonica*) to be effective against the fungi *Tyromyces palustris* (brown rot) and *Trametes versicolor* (white rot). The authors found that the treated wood also demonstrated resistance against the subterranean termite (*Coptotermes formosanus*). Thyme oil (extracted from *Thymus zygis*) is an essential oil that showed inhibitory effects against the decay fungi *Gloeophyllum trabeum*, *Postia placenta* and *Trametes versicolor* (Yang and Clausen 2007).

Bio-oils obtained by pyrolysis are rich in phenolic compounds and are expected to protect wood against fungi and insect degradation. Bio-oil can be considered as an alternative to creosote, having the advantage of not containing polynuclear aromatic hydrocarbons (PAH) that constitute health hazard. Examples of studies conducted on the use of pyrolysis oil for wood preservation are Kartal *et al.* 2004, Mansoor and Ali 1992, Mazela 2007, Meier and Faix 1999, Mourant *et al.* 2005 and Temiz *et al.* 2010. However, the main drawback of impregnated bio-oils is their leachability from wood (Temiz *et al.* 2010).

All the above investigations revealed the possible use of plant oils as a means of wood protection, and a general conclusion can be drawn that the main effect of plant and tall oils lies in the water repellency rather than in the oil's fungicidal properties. Understanding the mechanisms and modes of action by which wood can be protected using plant oils is the key to select the best technology and treatment.

1.4 Linseed and epoxidised linseed oils used for wood protection

Linseed oil (LO), also known as flaxseed oil, is obtained from the dried ripe seeds of the flax plant *Linum usitatissimum*. The flax plant is well-known because of the flax fibers used to make linen. The plant is extensively cultivated for its nutritional properties (table oil and seeds) and a great variety of other applications, *e.g.* as a component for wood treatments prior to painting.

LO is classified as a drying oil, which means it polymerizes by oxidation into a solid (relatively hard, though elastic) form in contact with air (oxygen). Thus, LO can improve dimensional stability and can protect wood against decay fungi by means of its water repellent (hydrophobic) properties. However, polymerization by oxidation takes extremely long time during which the oil can easily leach out of the treated wood when exposed outdoors (Koski 2008).

LO can be chemically modified to epoxidised linseed oil (ELO) which is a basic source for production of various plastics worldwide. Chen *et al.* (2002) reported that epoxidation of LO can be accomplished using three approaches: by using peraacetic acid, dioxirane, or hydrogen peroxide. However, the authors concluded that using hydrogen peroxide as oxidizing agent was the most efficient process and facilitated purification.

Few publications on the use of epoxidised oils for wood protection were found in the literature. Recent investigations on protective properties of ELO have been carried out (Panov *et al.* 2010, Terziev and Panov 2011, Temiz *et al.* 2013) and some promising results shown. For instance, Terziev and Panov (2011) reported anti-swelling efficiency (ASE) of wood within the range of 50-60%, with oil retentions of only 80 to 120 kg/m^3. Here the authors also found a significant improvement of wood durability in a laboratory decay test performed according to EN 113 (1997). The growth of the fungi *Trametes versicolor*, *Coniophora puteana*, *Postia placenta* and *Gloeophyllum trabeum* was significantly inhibited. It should also be noted that the wood mass loss was in the range of 10-15% compared to 20-30% of the untreated control samples - undoubtedly improvement but not far enough if the treated wood is intended for in-ground use. Even when polymerised, ELO can still act as a nutrient for microorganisms and insects. Temiz *et al.* (2013) carried out an insect test with larvae of the house longhorn beetle (*Hylotrupes bajulus*) and concluded that ELO (at 200 kg/m^3 retention) benefited the growth of larvae. The survival rate of the larvae was increased in the ELO treated wood compared to untreated wood.

At the time of writing this thesis, ELO treated Scots pine (*Pinus sylvestris*) sapwood samples are under evaluation in an above ground field test in Uppsala, Sweden. Some results have already been presented (Terziev and Panov 2011) for lap-joints treated with LO and ELO (at retentions of 96 and 76 kg/m^3 respectively). After 30 months (2.5 years) of exposure, the authors found that ELO (with lower retention than LO) demonstrated a significantly lower moisture absorption and adsorption compared to LO treated samples. The ELO treated wood kept an annual average MC of 18.7% while the LO treated samples demonstrated 10-25% higher moisture content. The authors also reported reduced occurrence of checks in both LO and ELO treated samples than in the untreated samples. Terziev and Panov (2011) reported as well an increase of the mechanical properties such as modulus of elasticity (MOE), modulus of rupture (MOR), impact bending strength and hardness of ELO treated wood. The authors used 20 samples and retentions of 100 and 200 kg/m^3 (rounded to the nearest hundred). The study showed a good correlation between the retention and the increase of MOE, MOR and hardness properties. MOE and MOR increased with 10-21% while hardness increased with up to 83%.

1.5 Existing problem

As already outlined, the study of Panov *et al.* (2010) described a modification treatment based on impregnation of wood with epoxidised linseed oil (ELO). The authors have studied and showed the hydrophobic properties of linseed oil (LO), ELO, tall oil ester and epoxidised tall oil ester by means of laboratory analyses and light microscopy studies. In the process of modification, a mixture of ELO and a catalyst (acetic acid) at strictly defined proportions was used. A significant drawback of the suggested technology is the *short usability time of the mixture, because the polymerization process starts immediately after the ELO and AA are mixed* and the viscosity of the impregnation mixture increases constantly with time. This process hampers practical applications due to problems with *e.g.* polymerization of the mixture in the treatment cylinder, pipes, pumps, etc., which can result in serious clogging of the entire system. Nevertheless, the technology has proven that the modified wood properties, *e.g.* dimensional stability, hydrophobicity and mechanical properties were improved significantly (Panov *et al.* 2010, Terziev and Panov 2011).

1.6 Objectives of the study

The main objective of the present study is to shed light on the dimensional stability, leachability and selected mechanical properties of wood impregnated with epoxidised linseed oil (ELO) by *means of a two-step process*. The process consists of impregnation of one ingredient (ELO or AA) in the first impregnation step and the other ingredient in the second step *to avoid polymerization of ELO prior to and under impregnation*. As mentioned, the catalyst triggers ELO polymerization directly on mixing with ELO. In a two-step process, when both ELO and catalyst mix in wood, clogging would be avoided without any significant risk for the impregnation system. Various treatment solutions for two-step processes were tested in the present study. Another objective of the work is to prove the polymerization of ELO in the wood cell wall.

The treated wood was subjected to comprehensive physical and mechanical testing to determine the characteristics of the modified material. Dimensional stability, strength, elasticity and ELO leaching were evaluated. Additional acetylated and heat-treated wood samples were included in the dimensional stability test for comparison purposes. Furthermore, Fourier transform infrared spectroscopy (FT-IR) analysis was used to determine the presence of polymerized ELO in the wood and as a fingerprint to prove whether the ELO was bound to the wood polymeric constituents.

2 Materials and methods

2.1 Sample preparation

Scots pine (*Pinus sylvestris* L.) sapwood was used throughout the study. Kiln dried stakes with dimensions of 25×50×500 mm (radial, tangential and longitudinal direction) were randomly selected. The selection was carried out with regard to the growth ring orientation which must be as parallel as possible to the tangential longitudinal face. However, small deviations had to be accepted due to the natural variability of wood. Cracked and pieces with knots were excluded. Since wood is an anisotropic material, to ensure the growth ring orientation as well as the symmetry of the stakes is key to achieving reliable dimensional stability results. The selected wood stakes were processed further to obtain samples for the planned treatments. Figure 1 depicts the sample preparation process.

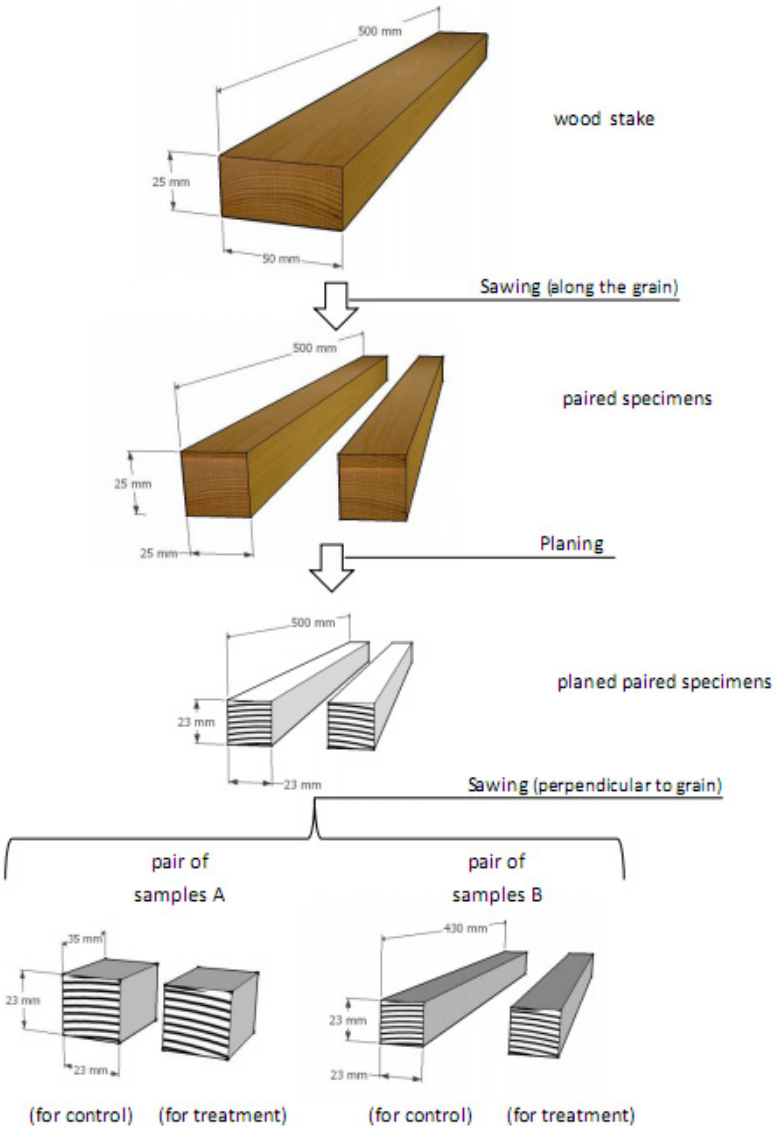

Figure 1. Illustration of sample preparation.

By sawing the wood stakes along the grain, two specimens were obtained (paired, each of dimensions 25×25×500 mm) that were chosen to be as similar as possible. The specimens were planed in a way that both radial and tangential dimensions were reduced to 23 mm. The samples were produced with the following method: the paired specimens were sawn

perpendicular to the grain at the same time. A sample from one of the specimens was then used as control, and the corresponding sample from the other specimen (located opposite to the first sample) was treated. This method aimed to make the samples for control and for treatment as identical as possible (Figure 1).

From the paired specimens, two types of samples were prepared, *i.e.* 'A' and 'B'. Samples A were used in the leaching and dimensional stability test, and samples B were used in the mechanical tests. The respective dimensions and the total number of samples prepared are shown in Table 1. The number of prepared samples was limited by the availability of material with appropriate characteristics and by the capacity of the impregnation autoclave.

Table 1. Sample dimensions in the three directions and number of samples prepared for treatments and control

Sample type	Dimensions [mm]			Number of samples	
	R	T	L	Control	Treated
A	23	23	35	158	158
B	23	23	430	108	108

Prior to the treatment procedure, the samples A were weighed and their dimensions measured. Three diagonals were marked with pencil on the faces of three sides (R, T and L) of samples A, defining the center of each face where the dimension measurements were done. Samples A were oven dried at 105ºC to constant dry weight, and their dimensions and weight recorded. Then, the samples were re-conditioned to constant mass at 20ºC and 65% relative humidity (RH) and once again their dimensions and weight recorded. Samples B were only weighed when conditioned at 20ºC and 65% RH prior to the treatment process. The sample weight was measured by a laboratory balance (Mettler, PM480 DeltaRange) with 0.001 g precision and dimensions by a caliper (Mitutoyo digimatic indicator, Absolute 543-464B) with 0.01 mm precision. In addition, thermally modified and acetylated wood samples were added to the dimensional stability test for comparative purposes.

2.2 Treatments

The employed sample treatment procedure is shown schematically in Figure 2. The wood samples were impregnated and afterwards cured. Four processes (indicated by numbers 1 to 4 inside red diamond-shaped symbols in Figure 2) were employed. Table 2 collates all treatments and summarizes several key aspects of the study.

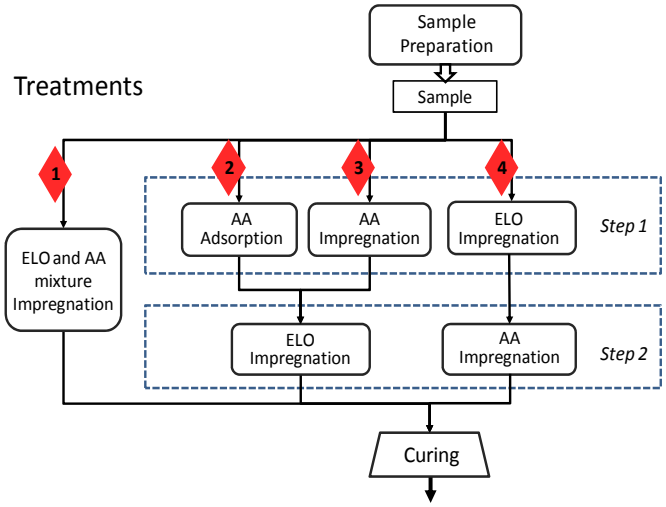

Figure 2. Schematic of the sample treatment procedure.

Chemicals

Epoxidised linseed oil with iodine number > 160 (ELO) was supplied by Traditem GmbH, Germany. The catalyst used was acetic acid of 99% purity (AA) obtained from VWR.

One-step process

In order to compare the results of already proven technology described by Panov *et al.* (2010) and Terziev and Panov (2011), *i.e.* impregnation with a mixture of ELO and pure AA at a ratio of 70:30 (process no. 1 in Figure 2), two trials were carried out. The trials had identical treatment parameters, however two trials were performed due to the low retention obtained in the first trial. These treatments are indicated with SE1 and SE2 (Table 2).

Two-step process

Step 1*: 1)* the wood was impregnated with AA using different concentrations (process no. 3 in Figure 2): pure (100%), 70, 50 and 30% diluted in water or *2)* the wood was impregnated with ELO (process no. 4 in *Figure 2*) or *3)* AA was introduced into the wood by adsorption (process no. 2 in Figure 2).

In *1)*, AA was impregnated in an autoclave using pressure (6 bars) and vacuum. Five batches were made using pure AA (100%) and diluted AA to concentrations of 70, 50, 30 and an additional 30% trial. The additional AA 30% concentration included 3% boric acid (BA) diluted in water.

In *2)*, the ELO was impregnated in an autoclave using pressure, temperature and vacuum. Prior to impregnation, the oil was preheated in a separated cylinder from the samples, then the samples were impregnated at 70ºC and 4 bars pressure and at the end the redundant ELO was extracted by vacuum.

In *3)*, samples A and B were placed in a container with a platform which separated the samples from the pure AA introduced at the bottom. The container was sealed and stored at room condition (20ºC) for 16 days. In this way, the samples subjected to an AA-vapour-saturated atmosphere adsorbed the catalyst.

Step 2*:* 1) for *1)* and *3)* in Step 1 (see above), the wood was impregnated with ELO; and 2) for *2)* in Step 1 (see above), the wood was impregnated with AA at 70% concentration.

For *1)* and *3)*, ELO was impregnated in an autoclave using pressure, temperature and vacuum. First, the oil was preheated in a separated cylinder from the samples, then the samples were impregnated at 70ºC and 4 bars pressure and the excess of ELO extracted by vacuum.

For *2)*, AA diluted with water to 70% concentration was impregnated in the autoclave using pressure (6 bars) and vacuum.

Target retention

The *target retention* (after impregnation) in the trials was always in the economically justified range of *80-150 kg/m*^{3}. Technically it is difficult to impregnate less than 70 kg/m^3; and higher retention would increase costs and product prices, as well as the density (and hence the weight) of the wood.

Treatment summary

Table 2 outlines the treatments performed, the treatment code that is used throughout this thesis and the number of samples used for each treatment. In addition, the specific parameters for each impregnation are found in Appendix 1.

Table 2. Treatments carried out in this study. For each treatment it is shown: a type-classification, regarding if the treatment is standard or novel; key-word description of the treatment; the treatment code, used throughout the study; and the number of samples A and B which were impregnated.

Treatment			No of samples	
Type	**Key-word description**	**Code**	**A**	**B**
Standard	1-step process – Mix. of ELO and AA (70:30 w/w)	**SE1**	18	12
Standard	1-step process – Mix. of ELO and AA (70:30 w/w)	**SE2**	18	12
Experimental	2-step process – 1st adsorbed AA + 2nd ELO	**Aad**	18	12
Experimental	2-step process – 1st AA at 100% + 2nd ELO	**A10**	18	12
Experimental	2-step process – 1st AA at 70% + 2nd ELO	**A7**	18	12
Experimental	2-step process – 1st AA at 50% + 2nd ELO	**A5**	18	12
Experimental	2-step process – 1st AA at 30% + 2nd ELO	**A3**	18	12
Experimental	2-step process – 1st AA at 30% & BA + 2nd ELO	**A3B**	18	12
Experimental	2-step process – 1st ELO + 2nd AA at 70%	**EA7**	14	12

Each batch produced was referred identically as the respective treatment throughout the study.

Curing

The impregnated samples were cured to facilitate and speed up polymerization of ELO. Samples A and B were cured separately. They were placed in two containers, each with a platform separating the samples from the pure AA introduced at the bottom. The containers were sealed and placed in two ovens to cure at various temperatures for various durations. *Table 3* shows the curing parameters used.

Table 3. Curing temperatures and durations used

Sample type	Duration [days]	Temperature [ºC]
A	14	70
B	20	50

After curing and prior to the characterization tests, samples were conditioned at 20ºC and 65% RH.

Degradation of wood polymers

The wood polymers (polysaccharides) more likely to be degraded by the treatments are hemicelluloses and the amorphous parts of cellulose. Degradation means that polymers are broken down by hydrolysis reaction into smaller chains or even down to single sugars (monosaccharides). These degraded polymers are likely to become separated from the wood structure and leached. In general, wood polymer degradation causes a decrease of some mechanical properties.

Wood structure damage could also be caused by the oligomers introduced by pressure into the cell wall or when extracted by vacuum.

Retention calculation

The chemical retention was calculated after every step and after the complete treatment. The retention is expressed in kg per cubic meter of wood (kg/m^3). The formulas used are specified below:

Steps 1 and 2

For samples A:

$$Retention_{Step-i} = \frac{W_{Step-i} - W_{Cond}}{V_{AD}} \quad (1)$$

where i corresponds to Step 1 or Step 2, W_{Step-i} is the weight after the corresponding step of the process, W_{Cond} is the conditioned weight before any treatment and V_{AD} is the absolute dry volume measured for each sample before any treatment.

For samples B:

$$Retention_{Step-i} = \frac{W_{Step-i} - W_{Cond}}{V_{Ref}} \quad (2)$$

where i corresponds to Step 1 or Step 2, W_{Step-i} is the weight after the corresponding step of the process, W_{Cond} is the conditioned weight before any treatment and V_{Ref} is a reference conditioned volume of 227.47 cm^3 used for all samples (before any treatment); corresponding to dimensions of 23×23×430 mm.

Note that, in the case of the one-step impregnation process (mixture of ELO and AA), the retention has been referred as in Step 2 treatment.

Complete treatment

For samples A:

$$Retention_{T-A} = \frac{W_{AD-T} - W_{AD-0}}{V_{AD-0}} \quad (3)$$

where W_{AD-T} is the absolute dry weight after the whole treatment, W_{AD-0} is the absolute dry weight before any treatment and V_{AD-0} is the absolute dry volume measured for each sample.

For samples B:

$$Retention_{T-B} = \frac{W_{Cond-T} - W_{Cond}}{V_{Ref}} \quad (4)$$

where W_{Cond-T} is the conditioned weight after the whole treatment, W_{Cond} is the conditioned weight before any treatment and V_{Ref} corresponds to the same reference conditioned volume used for all samples (before any treatment) as in Equation 2.

2.3 Leaching and dimensional stability test

Leaching and dimensional stability were tested by subjecting five samples of type A from each treatment and their corresponding control samples to 4 (four) cycles of water-soaking

and oven-drying (WSOD). In each cycle, the samples were water soaked in deionised water during the water-soaking phase, and oven dried in the oven-drying phase. Even though this test does not simulate conditions that wood would meet in service, it produces useful results regarding ELO leaching and wood dimensional stability.

Prior to the test, the samples were oven-dried and their weight and dimensions recorded.

The water-soaking phase consisted of: 1) putting the samples in a plastic container, covered by a plastic net with weights placed on top; 2) filling the container with deionised water making sure that all samples were submerged, while the net and the weights on top prevented the samples from floating; 3) after five days in water, the samples were taken out, their surfaces wiped gently with absorbent paper and their weight and dimensions recorded.

The oven-drying phase consisted of: 1) air-drying the samples for three days at room temperature (standard laboratory conditions) to avoid any possible hydrolysis of wood components; 2) the samples were oven-dried at 70ºC for two days; and 3) the samples were put into a desiccator and after cooling, their weights and dimensions recorded.

The data available for TM and AC wood samples were limited and thus, the analysis made was restricted to only their dimensional stability. Table 4 below describes in brief the treatment used, the code used throughout this thesis and the number of samples.

Table 4. Additional treatments, thermal modification and acetylation, included in the leaching and dimensional stability test of this study. For each treatment it is shown: a type-classification, regarding if the treatment is standard or novel; key-word description of the treatment; the treatment-code used throughout this thesis and the number of samples A and B

Treatment			No of samples	
Type	**Key-word description**	**Code***	**A**	**B**
Standard	Thermally modified wood (Thermowood D)	**TM**	4	-
Standard	Acetylated wood (22% WPG)	**AC**	4	-

** This code is used to refer to the treatments throughout the study.*

Analysis

Weights and dimensions of the samples measured at the various states made possible calculations of the following properties.

Weight percentage gain

Weight percentage gain (WPG) was calculated after the complete treatment (before leaching), WPG_T, and after leaching, WPG_{4C}, according to the following equations:

$$WPG_T = \left(\frac{W_{aT} - W_{bT}}{W_{bT}}\right) \times 100 \quad (5)$$

where, W_{aT} is the absolute dry weight of the sample after the complete treatment and W_{bT} is the absolute dry weight of the sample before treatment.

$$WPG_{4C} = \left(\frac{W_{4C} - W_{bT}}{W_{bT}}\right) \times 100 \quad (6)$$

where, W_{4C} is the absolute dry weight of the sample after the four (water-soaking-oven-drying) WSOD cycles and W_{bT} is the absolute dry weight of the sample before treatment.

The weight percentage gain (WPG) was always expressed in percentage (%).

Leached formulation

Leached formulation (LF) was calculated as the leached chemical in the WSOD cycles divided by the impregnated chemical before leaching. It was determined by the formulas presented below (Panov and Terziev 2009, Palanti *et al.* 2012):

$$LF = \left(\frac{WPG_T - WPG_{4C}}{WPG_T}\right) \times 100 = \left(\frac{W_{aT} - W_{4C}}{W_{aT} - W_{bT}}\right) \times 100 \quad (7)$$

where, the variables have the same meaning as previously shown and explained.

Leached formulation was also calculated for each of the WSOD cycles. The leaching in the first cycle LF_{1C} was defined as follows:

$$LF_{1C} = \left(\frac{W_{aT} - W_{1C}}{W_{aT} - W_{bT}}\right) \times 100 \quad (8)$$

where, W_{1C} is the absolute dry weight of the sample after the 1st WSOD cycle.
The leaching in cycles 2, 3 and 4 was calculated as follows:

$$LF_{iC} = \left(\frac{W_{(i-1)C} - W_{iC}}{W_{aT} - W_{bT}}\right) \times 100 \quad (9)$$

where *i* corresponds to the cycle number, *i.e.* 2, 3 or 4, W_{iC} is the absolute dry weight of the sample after the corresponding WSOD cycle and $W_{(i-1)C}$ is the absolute dry weight of the sample after the previous WSOD cycle.

Dimensional changes

Series of graphs plotting the volume and the states of the 4 WSOD cycles made it possible to analyse the trend of the volume changes by fitting two regression lines on the data of the water-soaked (WS) and the oven dried (OD) states. The regression lines were only performed on the data from the 2nd to the 4th cycles. The data of the 1st cycle were excluded since it has been well proven in the literature that the values obtained in this cycle are unrepresentative compared to the values obtained in the subsequent cycles (Hill 2006). In the 1st cycle, a significant volume of bulking chemical is highly susceptible to leaching by water and therefore a misinterpretation of the results can occur (Hill 2006).

In order to compare the results of the regression lines between the control samples and also between every treatment, alpha (α) and beta (β) angles and the regression coefficient (R^2) were used.

The alpha (α) angle is defined as the angle between the regression line and the horizontal axis (x-axis), thus being the slope of the regression line. It can be positive or negative indicating the volume change of the WS and OD states. The angle beta (β) is defined as the angle between the WS and OD regression lines and provides a measure of how parallel the

regression lines are. The smaller β is, the closer to parallel the regression lines. Figure 3 depicts the angles α and β.

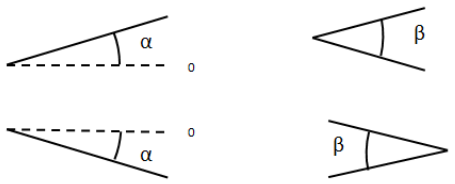

Figure 3. Illustration of alpha (α) and beta (β) angles. The alpha angle is the angle between the regression line (WS or OD) and the x-axis. The beta angle is the angle between the WS and OD regression lines and can only be positive; however, it indicates the parallelism of the regression lines.

Vectors expressing dimensional changes and anti-swelling efficiency were calculated according to Ohmae *et al.* (2002) methodology that is briefly described below.

Oven-dried dimensions before (t_o, r_o, l_o) and after (t_c, r_c, l_c) treatments were used to calculate the dimensional changes (T_c, R_c and L_c) caused by the treatment in the respective directions, as shown in the equations following:

$$T_c = \left(\frac{t_c}{t_0} - 1\right) \times 100 \tag{10}$$

$$R_c = \left(\frac{r_c}{r_0} - 1\right) \times 100 \tag{11}$$

$$L_c = \left(\frac{l_c}{l_0} - 1\right) \times 100 \tag{12}$$

Volumetric change (V_c) of wood after treatment was expressed by the vector C = (T_c, R_c) in the T-R coordinates, considering L_c negligible compared to T_c and R_c. The angle (θ_c) between C and the T-axis was calculated by the equation:

$$\theta_c = \tan^{-1}\left(\frac{R_c}{T_c}\right) \tag{13}$$

It is possible to evaluate the isotropy/anisotropy of the dimensional change by the angle θ_c. If θ_c equals 45º, then the dimensional change is isotropic ($R_c = T_c$).

Water-soaked dimensions of the 4th cycle for the untreated samples (t_s, r_s, l_s) were used to calculate the swelling coefficients in the three directions (T_u, R_u and L_u) for the untreated wood, as shown in the equations following:

$$T_u = \left(\frac{t_s}{t_0} - 1\right) \times 100 \tag{14}$$

$$R_u = \left(\frac{r_s}{r_0} - 1\right) \times 100 \tag{15}$$

$$L_u = \left(\frac{l_s}{l_0} - 1\right) \times 100 \quad (16)$$

Again the swelling coefficient L_u was considered negligible when compared to T_u and R_u, thus the volumetric swelling coefficient (V_u) can be calculated using only T_u and R_u.

Water-soaked dimensions of the 4th cycle for the treated samples (t_s, r_s, l_s) were used to calculate the swelling coefficients in the three directions (T_s, R_s and L_s) on basis of the oven-dried dimensions after treatment, as shown in the equations following:

$$T_s = \left(\frac{t_s}{t_0} - 1\right) \times 100 \quad (17)$$

$$R_s = \left(\frac{r_s}{r_0} - 1\right) \times 100 \quad (18)$$

$$L_s = \left(\frac{l_s}{l_0} - 1\right) \times 100 \quad (19)$$

The swelling coefficient L_s was considered negligible when compared to T_s and R_s, thus the volumetric swelling coefficient V_s can be expressed by the vector S = (T_s, R_s).

On the other hand, dimensional changes ($T_{s'}$, $R_{s'}$ and $L_{s'}$) for treated samples on basis of the oven-dried dimensions before treatment were calculated as shown in the equations following:

$$T_{s'} = \left(\frac{t_s}{t_u} - 1\right) \times 100 \quad (20)$$

$$R_{s'} = \left(\frac{r_s}{r_0} - 1\right) \times 100 \quad (21)$$

$$L_{s'} = \left(\frac{l_s}{l_0} - 1\right) \times 100 \quad (22)$$

The swelling coefficient $L_{s'}$ was considered negligible when compared to $T_{s'}$ and $R_{s'}$, thus the volumetric swelling coefficient $V_{s'}$ can be expressed only by the vector S' = ($T_{s'}$, $R_{s'}$). The angle ($\theta_{s'}$) between S' and the T-axis was calculated by the equation:

$$\theta_{s'} = \tan^{-1}\left(\frac{R_{s'}}{T_{s'}}\right) \quad (23)$$

It is possible to evaluate the isotropy/anisotropy of the volumetric swelling with $\theta_{s'}$. Identically as for θ_c, the dimensional change is isotropic ($R_{s'} = T_{s'}$) when $\theta_{s'}$ equals 45º.

The analysis above permits the dimensional stability of the treated samples to be evaluated using two anti-swelling efficiencies: ASE and ASE', which were calculated as shown in the equations following:

$$ASE = \left(1 - \frac{V_s}{V_u}\right) \times 100 \quad (24)$$

$$ASE' = \left(1 - \frac{V_{st}}{V_u}\right) \times 100 \quad (25)$$

Where:

$$V_u = T_u + R_u \quad (26)$$

$$V_s = T_s + R_s \quad (27)$$

$$V_{st} = T_{st} + R_{st} \quad (28)$$

It is important to note that the *ASE is based on the volumetric swelling of the treated samples on the basis of the oven-dried dimensions after treatment, while the ASE' is based on the volumetric swelling of the treated samples on the basis of the oven-dried dimensions before treatment.*

The higher the ASE, the higher dimensional stability achieved by the treatment. The ASE' provides different information depending on its value:

ASE' = 0 means that the treatment has only resulted in wood cell wall bulking by the ELO (ELO and wood polymers are not chemically bound).

ASE' > 0 means that the treatment has achieved chemical binding of the ELO to the wood polymers.

ASE' < 0 means that the wood polymeric constituents are damaged.

The higher or lower the ASE' values, the greater the effect.

2.4 Mechanical tests

The tests were performed on specimens at 12% MC (by conditioning at 20ºC and 65% RH). The mechanical tests were performed using a universal testing machine (Shimadzu, AG-X 50 KN). Measurement accuracy was ±0.01 mm for position, ±0.1% for speed and ±0.5% for loading. The specimens were prepared according to methods and general requirements for mechanical tests as recommended by ISO 3129 (1975).

Three-point bending test – modulus of elasticity and rupture (MOE and MOR)

The three-point bending test was used to determine the modulus of elasticity (MOE) and the modulus of rupture (MOR) on samples B, according to ISO 3349 (1975) and ISO 3133 (1975) respectively.

Brinell hardness

Test specimens with dimensions 23×23×70 mm (along the grain) were sawn from sound parts of the B samples (control and treated). The static hardness (Brinell) was determined perpendicular (on the radial surface) and parallel to grain according to ISO 3350 (1975) (results are presented independently).

Compression

Test specimens with dimensions 23×23×70 mm (along the grain) were sawn from sound parts of the B samples (control and treated). The compression stress parallel to grain was determined according to ISO 3787 (1976).

Analysis

For each mechanical property, a comparison between the results of the control and treated samples was made using box and whiskers plots. The percentage change in a mechanical property was calculated per sample, and mean and standard deviation (SD) are presented.

Statistical significant difference between control and treated samples for each mechanical property (long samples) was evaluated using the one-way analysis of variance test (ANOVA) with the program GNU Octave (version 3.2.3).

2.5 Fourier transform infrared spectroscopy

Infrared spectra of treated and untreated wood samples were obtained using the KBr (potassium bromide) technique on a Perkin-Elmer FT-IR Spectrum-100 spectrometer (resolution 4 cm^{-1}, 16 scan). Three samples from each treatment were ground together and oven dried. Three (3) mg of the obtained dry sawdust was dispersed in the matrix of 300 mg KBr and pressed to form a pellet. For analysis of ELO and polymerized ELO, the two KBr windows technique was used.

3 Results and discussion

3.1 Treatments

Impregnation

The retentions for each treatment and step of the impregnation process are shown in Table 5. Some samples had to be excluded because some defects (*e.g.* cracks) were detected either in the treated or in the corresponding control sample.

Table 5. Mean retentions after Steps 1 and 2 of the impregnation process for samples A and B

Treatment code	Samples A			Samples B		
	N	Retention $_{Step-1}$ [kg/m^3]	Retention $_{Step-2}$ [kg/m^3]	N	Retention $_{Step-1}$ [kg/m^3]	Retention $_{Step-2}$ [kg/m^3]
SE1	18	-	87	12	-	64
SE2	17	-	172	11	-	87
Aad	18	34	101	12	27	91
A10	18	188	74	11	119	125
A7	18	192	177	12	108	139
A5	18	157	247	12	92	136
A3	18	149	226	12	114	154
A3B	18	157	234	12	109	121
EA7	14	98	337	11	79	254

N indicates the number of samples.

Both SE1 and SE2 treatments (the method of Panov *et al.* 2010) showed lower retentions for samples B compared to A. An identical trend was observed for all the other treatments, except for A10 treatment. This could be explained by the longer time required for samples B to reach the same retention since these samples had larger volumes.

Under the same conditions, double retentions were obtained after the SE2 treatment compared to those after the SE1 treatment for samples A. This could not be explained by the higher viscosity of the ELO and AA mixture of the SE2 treatment, due to formation of oligomers after treatment SE1, since the same treating solution has been used for treatment SE2. Once impregnated, the oligomers are difficult to extract by the final vacuum of the process.

The retentions obtained after AA adsorbed in Step 1 for the Aad treatment were found to be very low (about 30 kg/m^3) for samples A and B. This indicates that the exposure time of 16 days was long enough for samples A and B to reach equilibrium acidic vapour content, *i.e.* they absorbed AA similarly. Accordingly, comparable retentions were obtained after impregnation in Step 2 with ELO for samples A (101 kg/m^3) and B (91 kg/m^3).

The A10, A7, A5, A3 and A3B treatments ensured fairly high retentions of AA in impregnation Step 1 for samples A and B, although again sample B showed lower retentions than sample A.

Surprisingly, low retentions were obtained for sample A after impregnation in Step 2 with the A10 and A7 treatments. In fact, for the A10 treatment, the retention decreased significantly (from 188 to 74 kg/m^3). An explanation for this may be that the AA impregnated in Step 1 had a degradable effect on wood cell wall polysaccharides (and even pits) resulting in a more porous wood structure and thus, a large volume of ELO was removed from the samples after

the post-vacuum following ELO impregnation; this might be the explanation of the low ELO retention. This must be a correct conclusion since a long time passed between AA and the ELO impregnation because the samples were stored sealed in a bag for about 12 h.

The A5, A3 and A3B treatments for A and B samples showed a more understandable tendency, *i.e.* the retentions increased after the impregnation (ELO) in Step 2. However, the initial retentions were higher than intended due to difficulties to impregnate the targeted AA.

Targeted ELO retentions were obtained in the EA7 treatment in the impregnation in Step 1, while relatively high AA retentions were attained in Step 2 (337 and 254 kg/m^3 for samples A and B respectively). It should be mentioned that technical difficulties and lack of experience with AA impregnation were the reasons for the excessive retentions achieved.

Complete treatment

The retentions for each treatment after completing the impregnation are presented in Table 6.

Table 6. Retentions, mean and standard deviation (SD), after complete treatment for samples A and B

Treatment code	Samples A			Samples B		
		Retention $_{T-A}$ [kg/m^3]			Retention $_{T-B}$ [kg/m^3]	
	N	Mean	SD	N	Mean	SD
SE1	13	92	15	12	78	7
SE2	12	148	14	11	107	16
Aad	13	116	13	12	90	14
A10	11	59	9	11	84	14
A7	13	106	28	12	87	27
A5	13	187	21	12	106	21
A3	6	170	10	12	101	23
A3B	11	172	27	12	72	14
EA7	10	222	40	11	144	21

N indicates the number of samples.

More detailed data of the retention figures for the complete treatment are presented in Table 29 (samples A) and Table 30 (samples B) in Appendix 2.

Several samples had to be excluded because the identification codes written on the samples were unreadable after treatment. On average, the number of samples A lost for each treatment was 6 samples when the treatments were completed. However, for A3 treatment there was a severe decrease in the number of suitable samples and only 6 out of 18 samples were appropriate for further use. For sample B, only 3 samples in the SE2, A10 and EA7 treatments were excluded.

For all treatments the retention was higher for sample A than for sample B, except in the A10 treatment, where this tendency was inverted.

For sample A, half of the retentions achieved were higher than the target retention. The A5, A3, A3B and EA7 treatments ensured higher retentions than 150 kg/m^3. The A5, A3 and A3B treatments used moderately or strongly diluted AA in water which may have affected the kinetic reaction in some manner. However, again the difficulties to achieve the target retention of AA must be taken into account. For sample B, retentions within the intended range (80-150 kg/m^3) were achieved.

Curing had another effect on the retentions of the treatments; moreover the effect was consistent for both A and B samples. For SE1, SE2 and Aad treatments, curing had negligible effect on the final retentions. A slight decrease in the retention was observed after curing for the A10, A7, A5, A3 and A3B treatments. It is expected that evaporation of residual AA during curing would result in reduced retentions. For the EA7 treatment, however, curing resulted in a significant reduction of retention (with approximately 110 kg/m^3). This is natural since AA was impregnated in Step 2 and thus, probably concentrated mainly on the wood surface; as a consequence, AA was easily evaporated during curing. Having about 200 kg/m^3 retention of AA in the wood, a 50% loss is relatively reasonable. The SE1 and SE2 treatments did not register any change in retention after curing because less AA was used and it was mixed with ELO. The same argument was valid for the Aad treatment.

A statistical summary over the retention results achieved after the complete treatment, for samples A and B is presented in Figure 4.

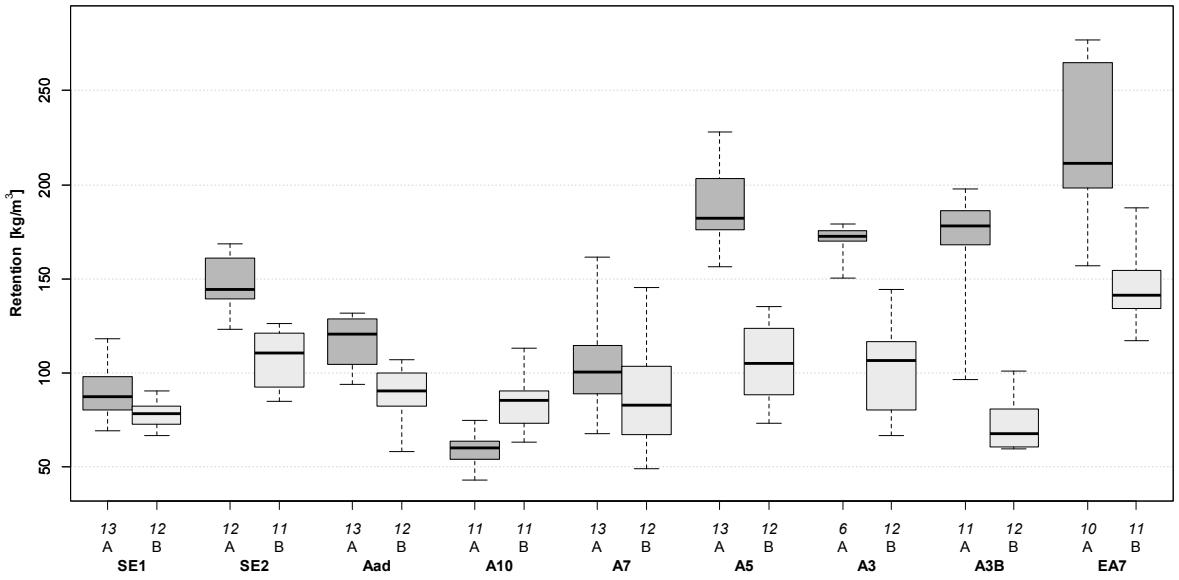

Figure 4. Retention (kg/m^3) per treatment, for both samples A (darker grey boxes) and samples B (lighter grey boxes). The retention is presented in the y-axis; while the x-axis shows: the treatment code, the letters A and B representing samples A and B respectively, and the number of samples.

The method described by Panov *et al.* (2010) has the drawback of slow polymerization of the ELO-AA mixture. On the other hand, the ELO and AA are mixed in an optimal proportion that is economically justified. The present study therefore demonstrated that the polymerization problem can be solved by a two-step impregnation process. However, it seems very difficult to achieve the optimal proportion between the ingredients and thus, they can be over-consumed. The natural variability of wood and the features of the proposed technology can probably lead to wider spread of the retentions in industrial conditions.

3.2 Leaching and dimensional stability test

The following results and interpretations must be treated with extreme caution since the changes in the external dimensions of the samples do not necessarily reflect changes in the cell wall volume (Hill 2006). In addition, only few samples were used for these tests.

Table 7 shows the absolute dry density and retention after the complete treatment for samples A selected for leaching and dimension stability test.

Table 7. Absolute Number dry density (mean and SD) before treatment, and retention (mean and SD) after complete treatment for the selected samples A

Treatment		Density [kg/m^3]		Retention $_{T-A}$ [kg/m^3]	
Code	**N**	**Mean**	**SD**	**Mean**	**SD**
SE1	5	545	28	107	10
SE2	5	500	28	161	8
Aad	5	508	25	129	3
A10	5	515	50	62	10
A7	5	521	30	117	24
A5	5	493	40	199	12
A3	5	502	16	174	4
A3B	5	515	19	188	8
EA7	5	512	36	238	38

N indicates the number of samples

Selected samples from A showed density values within the range of 493-545 kg/m^3 and SDs ranging from 16 to 50 kg/m^3. The Aad treatment with mean density of 508 kg/m^3 achieved a mean retention of 129 kg/m^3, while the EA7 treatment with mean density of 512 kg/m^3 achieved a mean retention of 238 kg/m^3. Another example is found in the A10 and A3B treatments, both with mean density of 515 kg/m^3 achieved very different retentions (62 and 188 kg/m^3 respectively). Observing the SD, the A10 treatment with a density SD of 50 kg/m^3 (greatest variability) showed a retention SD of 10 kg/m^3 (among the lower values). In this case, density does not correlate with the retention obtained by the treatments.

The retention values of the selected samples correlate to the retentions presented at complete treatment in the previous section. Since the thermally modified and acetylated samples were obtained from treated timber, no data were available about their initial density.

Water absorption-oven drying cycles

The average sample volume changes throughout the WSOD cycles for the control and treated samples are presented in Figures 5, 6 and 7. In order to compare all samples in identical test states, regression lines were calculated only based on the data of Cycles 2 to 4, although including as starting dry volume the previous OD state (OD_1). Figures 5, 6 and 7 are graphical illustrations of the volume dynamics for the untreated control, the SE2 and EA7 treated samples. The rest of the graphs for the treated samples are not shown to omit repetition and similarities; they can be found in Figures 18 to 24 in Appendix 3. Additional detailed analyses for all control and treated samples are shown in Tables 8 and 9.

<u>Control samples</u>

The average sample volume changes throughout the series of WSOD cycles, for *all* control samples, are presented in Figure 5.

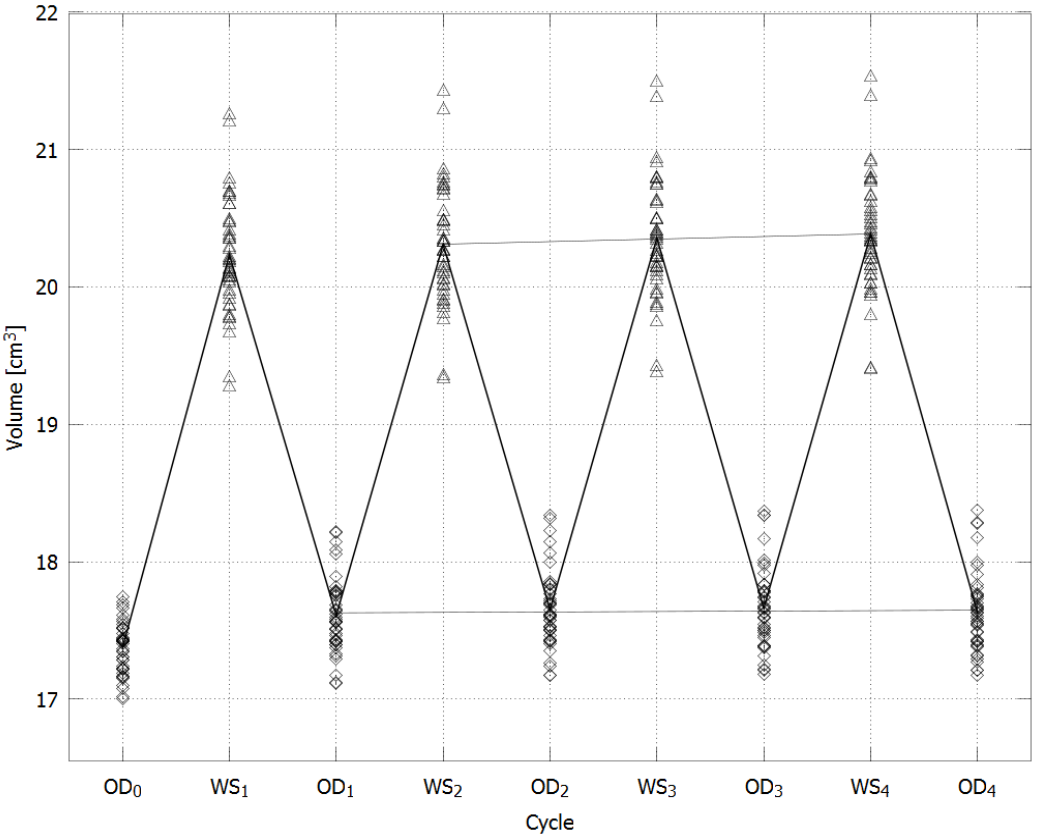

Figure 5. Water absorption-oven drying cycles for all control samples: the volume (cm^3) in each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). OD states are represented by diamond-shaped markers (not-filled) and WS states are represented by triangle-shaped markers (not-filled). The line going from the mean volume value of the first state to the mean volume value of next one until the last state represents the path followed by the samples during the series of cycles. The regression line fitting the data from states OD_1, OD_2, OD_3 and OD_4 represents the change in the OD volume of the samples. The regression line fitting the data from states WS_2, WS_3 and WS_4 represents the change in the WS volume of the samples.

It can be noted a difference between the first (OD_0) and the second (OD_1) absolute dry volumes, where the volume increased. This can be explained by the loss of extractives (by leaching) from the wood cell wall. Extractives are considered not to have any structural function in wood (Mantanis *et al.* 1995). However, Stamm and Loughborough (1942, cited by Mantanis *et al.* 1995) demonstrated that water-soluble extractives affect the shrinking and swelling of wood. The authors found that the extractives produce mechanical bulking in the cell wall and thus, the loss of extractives causes either a reduction in shrinkage or an increase in swelling.

Since OD_0 is an extreme of the data, it would greatly influence the OD regression line. The regression line analysis features (angle α and R^2) and the β angle are presented in Table 8. The Table shows the results of the control sample batches from the corresponding treatments (although the Figures are not presented) and the results of all control samples (presented in Figure 5) together.

Treatment SE2

Sample volume changes throughout the series of WSOD cycles for the SE2 treated samples are presented in Figure 6.

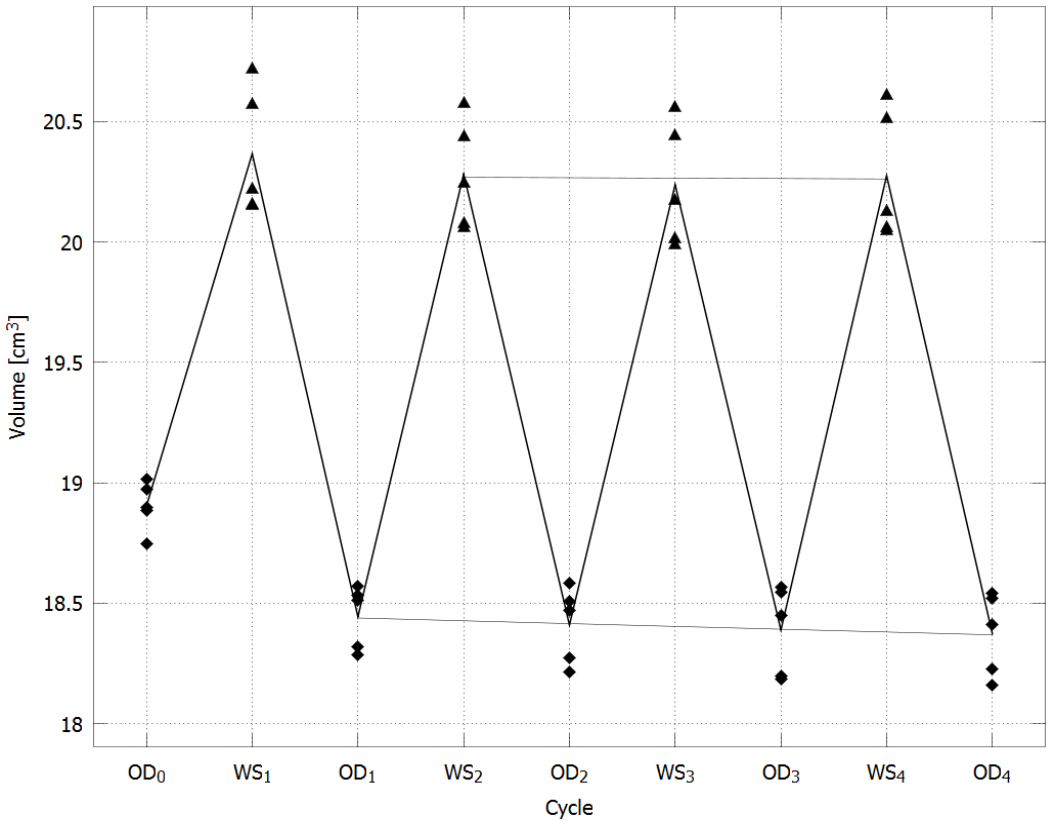

Figure 6. Water absorption-oven drying cycles for SE2 treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). OD and WS states are represented by diamond- and triangle-shaped markers respectively. The line going from the mean volume value of the first state to the mean volume value of next one until the last state represents the path followed by the samples during the series of cycles. The regression line fitting the data from the states OD_1, OD_2, OD_3 and OD_4 represents the change in the OD volume of the samples. The regression line fitting the data from the states WS_2, WS_3 and WS_4 represents the change in the WS volume of the samples.

Again, significant decreases in the volume of the samples were observed between the first and the second absolute dry state. This is mainly due to the leaching of non-polymerized ELO in the first WSOD cycle. Since it is an extreme of the data, this would considerably influence the OD regression line. The regression line plots (α angle and R^2) and the β angle are presented in Table 9.

Treatment EA7

The sample volume changes throughout the series of WSOD cycles for the EA7 treated samples are presented in Figure 7.

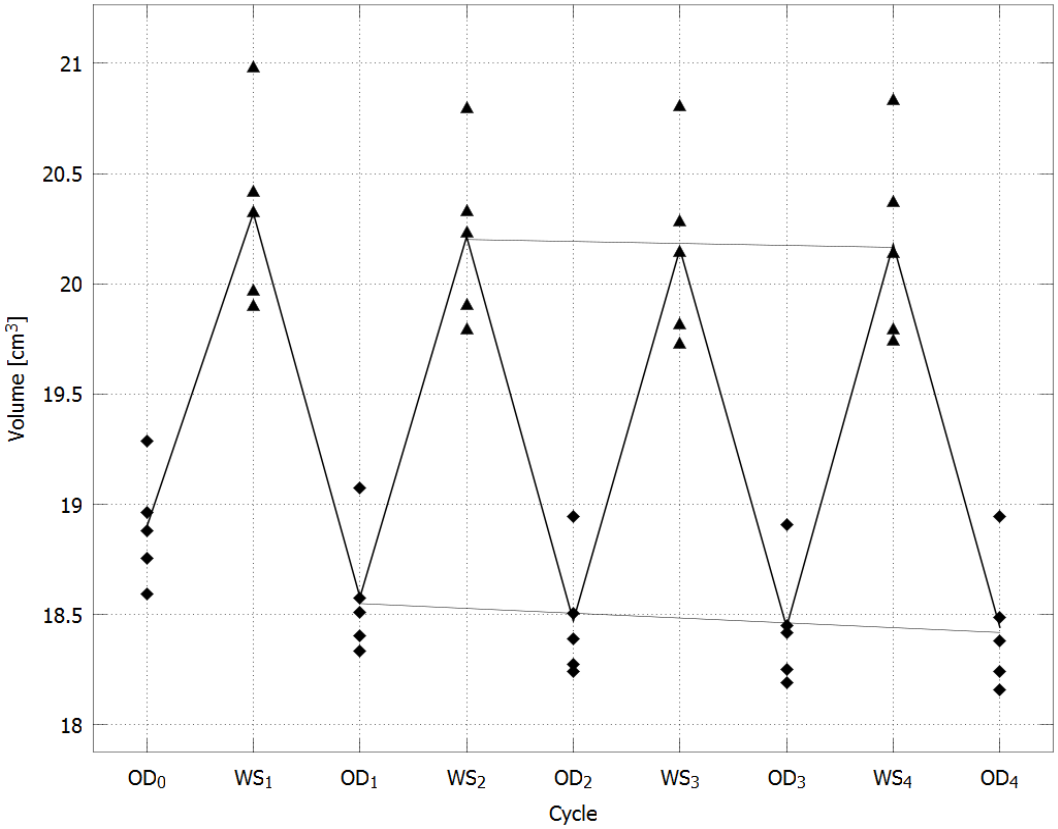

Figure 7. Water absorption-oven drying cycles for EA7 treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). Explanations of Figure are as in Figure 6.

Similar difference as in Figure 6 can be noted between the first to the second absolute dry volumes, where the volume decreases, and has the same explanation. This is a characteristic feature for all ELO treatments. Since it is at an extreme of the data, this would heavily influence the OD regression line. The regression line analysis results, the angles (α and β) and the correlation coefficient (R^2), are presented in Table 9.

Analyses of the volume change throughout the series of WSOD cycles are collated in Tables 8 and 9 for all control and treated samples respectively. The regression lines fitting the data of the OD and WS states are referred as OD and WS regression lines respectively. For each of the regression lines it is shown: 1) the $\boldsymbol{\alpha}$ angle; 2) its corresponding symbol, indicating negative or positive slope and 3) the regression coefficient (R^2). Moreover, the Tables show the $\boldsymbol{\beta}$ angle indicating parallelism and its corresponding symbol, indicating if the angle is opening to increasing volume change or closing to decreasing volume change.

Even though, only Figure 5 for all control samples is presented, the regression lines, their angles and R^2 were calculated for each of the control sample batches corresponding to each treatment. The results are collated in Table 8.

Table 8. OD and WS regression coefficients, α and β angles for the control untreated samples

Control samples corresponding treatment code	OD Regression Line			WS Regression Line			Beta angle	
	Alpha angle		R^2	Alpha angle		R^2		
	symbol	[º]		symbol	[º]		symbol	[º]
SE1		0.07	0.0002		0.80	0.0016		0.73
SE2		0.08	0.0019		1.03	0.0089		0.95
Aad		-0.57	0.0126		0.33	0.0016		0.90
A10		0.92	0.0163		0.77	0.0014		0.15
A7		0.52	0.0106		0.15	0.0004		0.37
A5		0.36	0.0083		2.56	0.0495		2.20
A3		-0.58	0.0227		1.40	0.0127		1.98
A3B		0.80	0.0740		0.59	0.0080		0.21
EA7		0.03	0.0000		1.90	0.0358		1.87
All Control		**0.18**	**0.0007**		**1.06**	**0.0051**		**0.88**

As can be seen in Table 8, only untreated samples corresponding to the Aad and A3 treatments have a negative value of α angle indicating a decrease in the oven-dry volume per cycle, while the most of the other control samples show an increase in the oven-dried volume per cycle. The water-soaked volume however increases for all control samples.

The β angle describes the parallelism between the two regression lines. The control samples corresponding to the SE1, SE2 and Aad treatments have a slightly open beta angle indicating a small loss of cell wall bulking extractives. For the SE1 and SE2 treatments the oven-dried volume increases while for the Aad treatment there is a decrease in oven-dried volume.

The control samples corresponding to the A5, A3 and EA7 treatments have a relatively wide β angle indicating a more significant loss of cell wall bulking extractives. This can cause a decrease in dimensional stability.

The control samples corresponding to A10, A7 and A3B treatments have a very small and negligible β angle indicating that the test does not cause loss of cell wall material nor cell wall extractives.

In general, for the control samples, a β angle ranging from 0 to 1º can probably be considered as an acceptable result given the presented variability within wood. In conclusion, these results indicate that most likely the treated samples of the A5, A3 and EA7 treatments have lower initial (before treatment) dimensional stability than the others (followed by the treated samples in the SE1, SE2 and Aad treatments).

Table 9. OD and WS regression lines results and the beta angle for the treated samples

Treatment Code	OD Regression Line			WS Regression Line			Beta angle	
	Alpha angle		R^2	Alpha angle		R^2		
	symbol	[º]		symbol	[º]		symbol	[º]
SE1		-0.60	0.0310		0.44	0.0010		1.04
SE2		-0.67	0.0309		-0.10	0.0001		0.57
Aad		-0.69	0.0292		0.41	0.0017		1.10
A10		0.11	0.0010		0.86	0.0026		0.75
A7		-0.40	0.0017		-0.54	0.0016		0.13
A5		-0.82	0.0718		-1.05	0.0100		0.23
A3		-0.38	0.0072		-0.63	0.0033		0.26
A3B		-0.81	0.0732		-0.13	0.0002		0.69
EA7		-1.25	0.0336		-0.51	0.0015		0.74

Samples from the SE1 and Aad treatments seem to behave in the same manner regarding the OD and WS regression coefficients. A decrease of the oven-dried volume (α = -0.60º and α = -0.69º) and an increase of the water-soaked volume (α = 0.44º and α = 0.41º) resulted in wide β angles of 1º (rounded to the nearest unit), indicating a significant loss of the cell wall cross-linking ELO. The loss of ELO leads to decreased dimensional stability (Hill 2006).

Samples from the SE2 and A3B treatments showed a similar behaviour. A decrease of the oven-dried volume (α = -0.67º and α = -0.81º) and a very small or null decrease of the water-soaked volume (α = -0.10º and α = -0.13º) resulted in β angles of 0.57º and 0.69º. This denotes a smaller loss of the cell wall cross-linking ELO than the previously mentioned treatments though still significant, which implies a decrease in dimensional stability.

Samples from the A10 treatment show very different tendency when compared to the others. It is the only treatment which OD regression line does not decrease (α = 0.11º) meaning that there is no reduction in the oven-dried volume while an increase of the water-soaked volume (α = 0.86º) was observed. This resulted in an opening β angle of 0.75º. The tendency contrasts that of SE2 and A3B treatments, although the interpretation of the results is a significant loss of the cell wall cross-linking ELO.

Samples from the EA7 treatment shows the highest decrease of the oven-dried volume, α is -1.25º and a decrease of the water-soaked volume ($\alpha \approx$ -0.51º) resulting in an opening β angle of 0.74º (very similar to that of the A10 treatment).

Samples from the A5 treatment show a decrease in the oven-dried volume, α = -0.82º, and the highest decrease of the water-soaked volume (α = -1.05º) resulting in a closing β angle of 0.23º (very small angle, similar to those of the A7 and A3 treatments).

Samples from the A7 and A3 treatments seem to show a very similar behaviour regarding the OD and WS regression coefficients. A decrease of the oven-dried volume (α = -0.40º and α = -0.38º) and a decrease of the water-soaked volume (α = -0.54º and α = -0.63º) result in closing β angles of 0.13º and 0.26º.

The variety of results for the treated samples above can be summarized and interpreted to two ways:

1) Both water absorption and oven drying volumes *decrease* proportionally. This indicates loss of water soluble extractives and some fragments of the polysaccharides

(single sugars or oligomers) that have been produced by the action of e.g. catalyst, process parameters, etc. At the same time there *is no loss of the modifying agent.* Examples of such treatments in Table 9 are SE2, A7, A5, A3, A3B and EA7. These treatments guarantee a reliable modification of the wood call wall and hence, high dimensional stability.

2) Water absorption volumes *increase* while oven drying volumes decrease. This case indicates *loss of the modifying agent* and, additionally, extractives and carbohydrates. Examples of such treatments in Table 9 are SE1 and Aad. These treatments are example of less successful modification, *i.e.* less modifying agent in the wood cell wall and/or less bonds to the wood hydroxyl groups. Naturally, this leads to lower dimensional stability.

As already mentioned, β is a measure of parallelism between the WS and OD regression lines and *indicates the trend of volume increase or decrease in the next cycles.* For instance, for the SE1, Aad and A10 treatments, β angle is open to right, *i.e.* continuous modification agent loss. The A7, A5 and A3 treatments in which β angle is open to left, are examples of treatments where sample volumes are getting close to constant. The interpretation above should be seen critically because the values of the β angles are about 1º or less, *i.e.* negligible.

Weight percentage gain

Weight percentage gain (WPG) results for each treatment are shown in Figure 8. WPG_T (after the complete treatment and before leaching) and WPG_{4C} (after leaching in the four WSOD cycles) are presented.

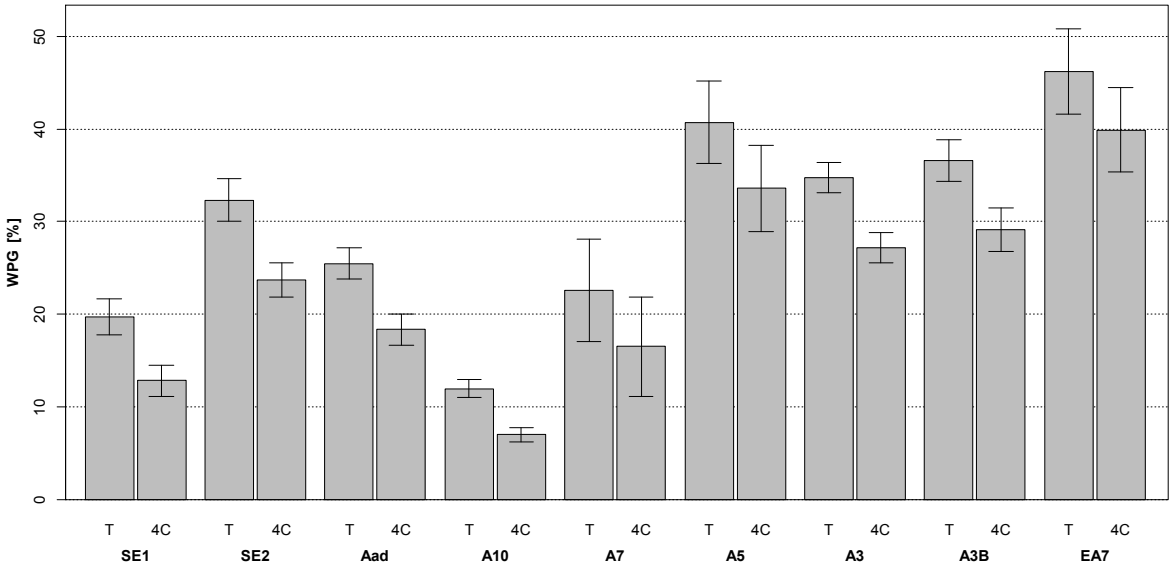

Figure 8. WPG before and after the leaching test. The figure shows WPG_T and WPG_{4C} for each treatment, determined as a mean of 5 samples used in the leaching test. The bars represent mean values; the error bars represent the standard deviation (SD). The x-axis shows the treatment code and the key letters T and 4C representing the WPG for a complete treatment (WPG_T) and after the 4th WSOD cycle (WPG_{4C}) respectively.

As can be seen from Figure 8, there is a decrease in WPG after leaching for all treatments. Table 10 shows the decrease in WPG, which varies from 5.0 to 8.6% on average.

Table 10. Decrease in WPG during the leaching test

Treatment		Decrease in WPG [%]	
Code	**N**	**Mean**	**SD**
SE1	5	6.9	0.4
SE2	5	8.6	0.7
Aad	5	7.1	0.2
A10	5	5.0	0.3
A7	5	6.1	0.5
A5	5	7.1	0.2
A3	5	7.5	0.2
A3B	5	7.5	0.2
EA7	5	6.3	0.3

N indicates the number of samples.

In order to compare the treatment retentions, SE2's gains (WPG_T = 32% and WPG_{4C} = 23%) were considered as reference results, since it was proven as a successful treatment with a mixture of ELO and AA (Panov *et al.* 2010). Thus, WPGs of SE1, Aad, A10 and A7 treatments were found to be below the reference, while A5, A3, A3B and EA7 WPG's were above the reference. A10 treatment shows the lowest WPG results, followed by SE1, A7 and Aad treatments. Above the SE's WPGs the A3 treatment WPG shows the lowest results followed by those of the A3B, A5 and EA7 treatments.

It should be mentioned that during the Aad, A10 and A7 treatments, the samples were pre-heated with AA inside the chamber (while ELO was pre-heating prior to impregnation). This should certainly affect the results since AA is known to degrade the wood carbohydrate (Vázquez and Lage 1992). Within the experimental treatments, both when ELO was impregnated in Step 1 or in Step 2 show WPGs above the SE's. However, the WPGs for the EA7 treatment stand out, with mean values of about 45% (WPG_T) and 40% (WPG_{4C}). The highest WPG variations (SD) can be found in the A7, A5 and EA7 treatments.

Leached formulation

Leached formulation (LF) results per cycle, for each treatment are shown in Figure 9.

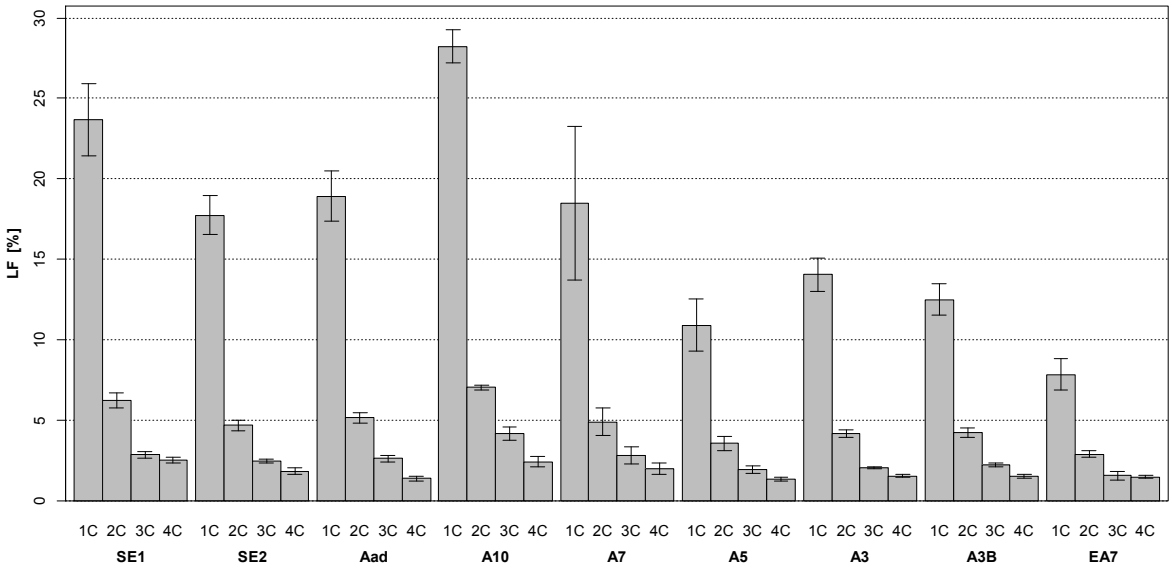

Figure 9. Leached formulation (LF) between each OD state during the WSOD test. The bars represent mean values and the error bars represent the SD. The x-axis shows the treatment code and the key letters 1C, 2C, 3C, and 4C represent the LF for every cycle.

The LF levels of the treatments were inversely proportional to corresponding WPG results; the higher the WPG the lower LF (at every cycle), which is an expected relationship. In cycles 1 and 2 most of the leaching likely came from the free agent on the surface of the wood, and rays, resin canals and lumens in the wood.

The LF difference between cycles 3 and 4 probably indicates the level of interaction (modification) between the ELO and the wood polymeric components. Thus, a larger difference means that the strength of the interaction was weaker in cycle 3 than in 4, and a smaller difference means a more equal strength of the interaction. This gives an idea of the stability of the modification (how fixed the ELO was). The Aad and A10 treatments show a larger LF between cycles 3 and 4 than the other treatments, possibly indicating a less consolidated modification.

Anti-swelling efficiency

An overall presentation of the calculated anti-swelling efficiency of the studied treatments is presented in Table 11. The principle calculations are shown in the material and methods. It should be emphasized that the classical *ASE* was calculated on basis of the oven-dried dimensions *after the treatment*, while the *ASE'* was calculated on basis of the oven-dried dimensions *before the treatment*.

The higher the ASE, the higher dimensional stability achieved by the treatment. The ASE' provides different information and depends on its value as follows:

ASE' > 0 means that the treatment has achieved chemical binding of the ELO to the wood polymers.

ASE' < 0 means that the wood polymeric constituents are damaged.

The higher or lower the ASE' values are, the greater the effect.

Table 11. Results for each treatment and treated sample namely, WPG_T, leached formulation (LF), dimensional change vectors (C, S' and S), the angle between S' and T-x-axis (θ s'), ASE' and ASE

Treatment code	WPG_T [%]	LF [%]	C=(Tc, Rc) ([%], [%])	S'=(Ts', Rs') ([%], [%])	θs' [º]	ASE' [%]	S = (Ts, Rs) ([%], [%])	ASE [%]
	20.7	35.1	(3.6, 2.0)	(10.5, 5.0)	25.3	-14.5	(6.7, 2.9)	29.3
	16.6	34.6	(3.0, 2.4)	(10.2, 6.2)	31.4	6.6	(7.0, 3.7)	39.1
SE1	21.0	35.5	(4.2, 2.3)	(10.1, 4.1)	22.2	-9.8	(5.7, 1.8)	42.9
	21.3	27.4	(3.8, 2.3)	(9.7, 3.9)	21.7	-6.1	(5.7, 1.5)	43.8
	18.9	25.0	(3.1, 2.3)	(10.4, 5.7)	28.6	-0.4	(7.1, 3.3)	35.1
	28.8	26.1	(3.5, 2.9)	(10.1, 6.4)	32.6	2.0	(6.4, 3.5)	41.6
	33.3	26.4	(4.4, 3.0)	(11.1, 5.3)	25.6	-10.3	(6.4, 2.2)	41.7
SE2	34.5	28.6	(4.2, 2.5)	(9.0, 3.6)	22.0	8.5	(4.6, 1.1)	58.7
	31.1	35.1	(4.1, 2.8)	(9.3, 3.7)	21.7	3.1	(5.0, 0.9)	56.2
	33.7	34.6	(4.5, 2.6)	(9.4, 3.6)	21.0	3.5	(4.7, 1.0)	57.9
	24.5	29.4	(3.8, 3.0)	(11.7, 6.9)	30.5	-6.0	(7.6, 3.8)	35.1
	28.1	25.7	(4.1, 2.0)	(11.5, 4.6)	22.0	0.5	(7.0, 2.5)	40.7
Aad	23.8	30.5	(4.1, 2.4)	(11.5, 6.1)	27.9	1.3	(7.1, 3.6)	40.1
	25.7	27.2	(3.5, 2.6)	(9.8, 5.6)	29.7	2.8	(6.1, 2.9)	43.2
	25.2	27.4	(3.3, 2.5)	(10.4, 5.6)	28.1	2.1	(6.9, 2.9)	39.9
	12.9	40.9	(3.5, 2.8)	(10.2, 5.8)	29.7	15.3	(6.5, 2.9)	50.4
	12.1	43.2	(4.1, 2.9)	(11.9, 6.3)	28.0	-20.1	(7.4, 3.3)	28.8
A10	12.6	40.1	(3.1, 3.5)	(11.0, 7.9)	35.8	7.3	(7.6, 4.2)	41.7
	11.8	41.1	(2.8, 2.6)	(7.5, 4.6)	31.7	3.5	(4.6, 2.0)	47.3
	10.4	43.8	(2.5, 2.6)	(7.2, 4.6)	32.4	6.8	(4.6, 1.9)	49.0
	20.1	28.7	(3.7, 4.4)	(10.2, 7.3)	35.4	-14.5	(6.3, 2.8)	40.7
	27.9	24.7	(5.5, 3.5)	(11.5, 5.5)	25.7	3.3	(5.7, 1.9)	56.9
A7	20.7	30.3	(4.9, 2.7)	(11.4, 5.1)	24.3	2.6	(6.2, 2.4)	49.4
	15.6	37.0	(3.8, 2.1)	(10.8, 5.1)	25.1	-3.8	(6.8, 2.9)	36.8
	28.5	19.9	(5.0, 4.7)	(11.6, 7.4)	32.4	-16.1	(6.3, 2.5)	46.0
	44.9	15.3	(4.0, 2.5)	(10.1, 4.4)	23.4	7.1	(5.9, 1.8)	50.7
	45.9	15.1	(4.5, 2.7)	(10.4, 4.8)	24.9	1.1	(5.6, 2.1)	49.7
A5	39.2	19.0	(4.9, 3.5)	(11.3, 6.4)	29.5	4.0	(6.1, 2.9)	51.5
	36.0	19.6	(4.0, 3.3)	(9.0, 5.1)	29.7	0.1	(4.7, 1.7)	54.1
	37.5	19.6	(5.3, 3.5)	(11.8, 6.4)	28.6	-3.1	(6.2, 2.9)	48.9
	37.0	20.1	(5.1, 3.0)	(8.7, 4.5)	27.1	-4.2	(3.5, 1.4)	61.6
	35.7	21.8	(4.1, 3.1)	(10.1, 6.0)	30.7	-4.5	(5.7, 2.8)	44.8
A3	33.7	22.9	(5.9, 3.3)	(11.6, 5.6)	25.6	5.9	(5.4, 2.2)	57.9
	32.7	22.2	(4.9, 2.9)	(10.5, 5.4)	27.0	-14.2	(5.3, 2.4)	44.3
	34.5	21.8	(3.8, 3.4)	(10.4, 6.5)	32.1	-5.3	(6.4, 3.0)	41.7
	34.4	22.5	(4.4, 2.2)	(10.3, 4.9)	25.4	0.4	(5.6, 2.6)	45.8
	37.1	20.3	(4.5, 3.4)	(10.6, 5.9)	29.2	-2.4	(5.8, 2.2)	48.8
A3B	34.0	21.4	(5.3, 2.6)	(10.7, 4.8)	24.3	4.6	(5.1, 2.1)	55.4
	38.9	18.8	(5.2, 2.5)	(9.8, 4.6)	25.5	1.2	(4.4, 2.1)	55.4
	38.4	19.3	(4.7, 2.7)	(9.9, 5.1)	27.0	2.1	(5.0, 2.3)	52.4
	41.8	15.7	(5.4, 3.3)	(11.2, 4.8)	23.1	4.4	(5.5, 1.5)	58.4
	42.5	14.3	(4.7, 2.9)	(10.7, 5.3)	26.3	2.6	(5.8, 2.3)	50.8
EA7	51.0	13.0	(4.3, 3.4)	(8.7, 5.7)	33.3	7.3	(4.2, 2.3)	58.0
	51.2	12.2	(4.7, 3.4)	(8.9, 5.2)	30.3	7.4	(4.0, 1.8)	62.1
	44.4	13.4	(4.6, 3.1)	(10.2, 5.8)	30.1	6.4	(5.2, 2.7)	53.6

Table 11. Continuation

Treatment Code	WPG_T [%]	LF [%]	C=(Tc,Rc) ([%], [%])	S'=(Ts',Rs') ([%], [%])	θs' [°]	ASE' [%]	S = (Ts,Rs) ([%], [%])	ASE [%]
HT	- *	-	(-1.0, -0.1)	(5.8, 3.0)	27.6	46.7	(6.8, 3.1)	39.5
	-	-	(-1.6, -0.6)	(5.3, 2.9)	28.4	48.3	(7.1, 3.5)	33.5
	-	-	(-2.7, -0.3)	(3.8, 3.2)	40.6	56.9	(6.7, 3.6)	37.0
	-	-	(-1.5, 0.0)	(5.4, 3.4)	32.2	46.3	(7.0, 3.4)	36.4
AC	-	-	(5.8, 4.2)	(8.1, 5.1)	31.9	19.7	(2.3, 0.9)	80.9
	-	-	(5.4, 8.6)	(7.6, 9.3)	50.7	-6.5	(2.1, 0.6)	83.0
	-	-	(12.7, 8.3)	(15.1, 9.6)	32.3	-51.5	(2.1, 1.1)	80.1
	-	-	(9.7, 4.3)	(12.3, 5.9)	25.7	-12.2	(2.4, 1.6)	75.8

** Lack of recorded weights prior to the treatment made the calculation of these parameters impossible.*

Based on the findings of these tests, it is concluded that *ELO treatments ensure the wood an improved dimensional stability that is comparable or even better than that achieved by thermal modification*. It was also observed that the impregnation of AA in first step results in wood degradation which was countered by later polymerization of ELO in the second impregnation step. Thus, the best practice would be impregnation of oil in Step 1 followed by impregnation of catalyst in Step 2 in order to minimize wood carbohydrate hydrolysis. Another important observation was that the ASE' calculations do not always reflect the real phenomenon that occurred during the treatments (the reasons for this are given in the first paragraph of section 3.2).

With retentions of 80 to 120 kg/m^3, the anti-swelling efficiency (ASE) reported by Terziev and Panov (2011) was within the range of 50-60%. In this study, the SE2 treatment (retention ≈ 160 kg/m^3) showed ASE within the range of 42-59%. The EA7 treatment (retention ≈ 240 kg/m^3) showed ASE within the range of 51-62%. These facts support the findings of Panov *et al.* (2010); at the same time the ASE has very small or negligible correlation with the retention.

Figure 10 compares the studied ELO treatments by using the ASE and ASE' results calculated in Table 11.

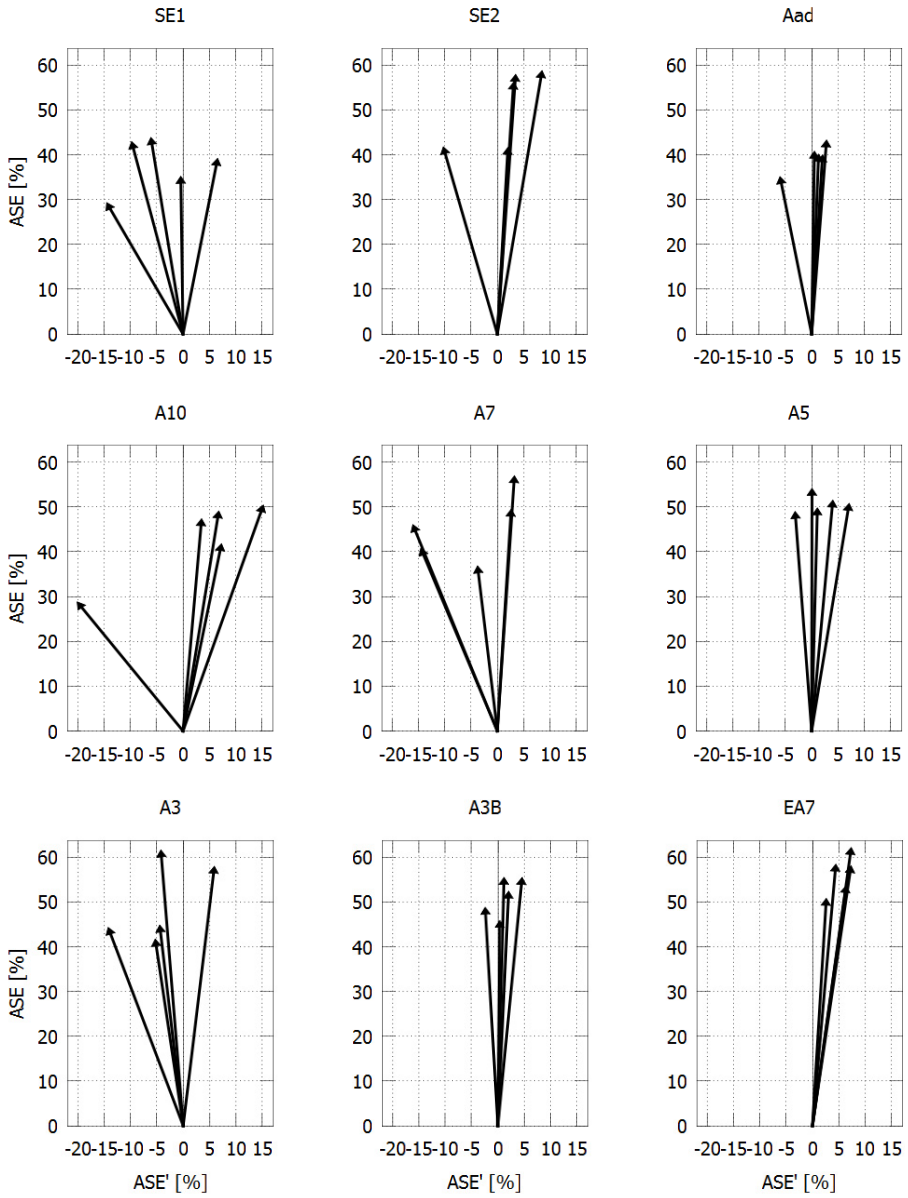

Figure 10. Graphs representing the results of the treatment specified by plotting the vectors (one for each sample) with coordinates of ASE (%) and ASE' (%).

Considering the ASE and ASE' values and the uniformity of these results, it is possible to rank the studied treatments. The best results using ELO were achieved in the EA7 treatment, with the highest ASE, fairly high ASE' and very uniform values. The second best results are from the SE2, A5 and A3B treatments; only one sample showed a negative ASE', the samples demonstrated high ASE and have acceptable uniformity. The A10 treatment showed the highest and lowest ASE', however only one sample has negative ASE'. The Aad treatment showed low ASE, however the results are very uniform and only one sample has negative ASE'. The results of the SE1, A7 and A3 treatments could be considered worst. They have three to four samples with negative ASE' values on average low ASEs and low uniformity.

Regarding the SE1 treatment, the low ASE obtained could be explained most likely by the low percentage gain obtained in this case. The negative ASE' may be explained by the damage of wood polymers induced by impregnation of ELO oligomers.

For the SE2 treatment, the low ASE obtained in general was in agreement with previous findings (Panov *et al.* 2010, Terziev and Panov 2011) and may be explained by the polymerization of ELO in the wood cell wall, as was shown by the positive trend of ASE'. The negative ASE' of one of the vectors may be explained by the wood natural variability and the heterogeneity of the technology used (*i.e.* location of the samples in the autoclave together with the parameters applied).

The ASE for the Aad treatment is on average equal to the ASE of the SE1 treatment and may be explained by the low retention of AA achieved in Step 1. It is presumed that the amount of AA inside the wood was not enough for polymerization of ELO to the wood polymeric constituents. However, the eventual damage caused by the long exposure of the samples to AA saturated atmosphere seemed to be counteracted by subsequent polymerization of ELO. The negative ASE' obtained for one of the vectors may be explained by the same reasons as stated for the SE2 treatment.

The same explanation is valid for all treatments in which AA was impregnated in the first step; after the impregnation of samples with pure AA in Step 1, some part of the carbohydrates was degraded, but this effect was successfully countered by later impregnation and polymerization of ELO in Step 2. This effect can be seen with one of the samples with lowest negative ASE'.

For the A3 treatment, the great variation of ASE (40-60%) may be explained by the same reasons as stated for the SE2 treatment. The retentions at complete treatment (or WPG) of the samples of the A3 treatment are the lowest among the A5, A3 and A3B treatments, which may partially explain the low ASE value. The ASE' results are fairly negative, indicating damage of the wood polymeric constituents.

For the A3B treatment, the ASE and ASE' results show good polymerization of the ELO in the wood cell wall and very little cell wall damage, if any (due to negative vector considered as in the SE2 treatment).

Figure 11 compares the TM and AC treatments by using the ASE and ASE' results.

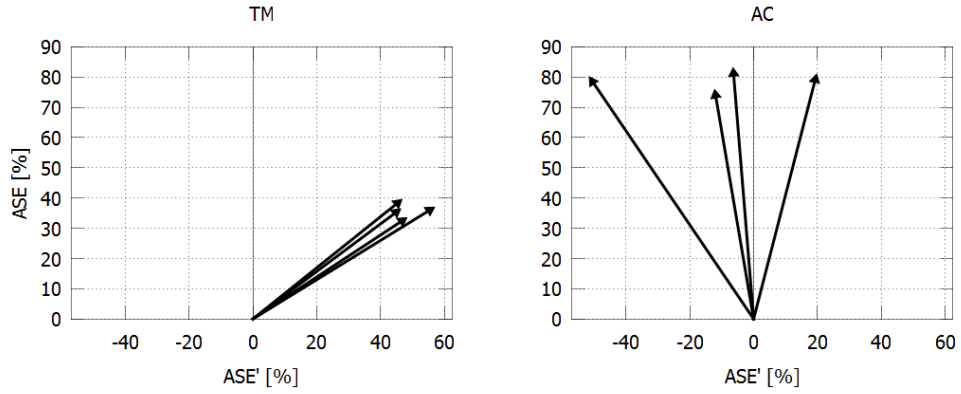

Figure 11. Graphs representing the results of the TM and AC wood by plotting the vectors (one for each sample) with coordinates of ASE (%) and ASE' (%).

It is well known that during thermal modification of wood, AA liberated from hemicelluloses, catalyses further carbohydrate cleavage causing a reduction of the degree of polymerization of carbohydrates, with additional formation of new ether linkages between the lignin units in

high temperatures taking place. Thus, the obtained values of ASE' for TM samples do not reflect the real phenomenon that occurred in the cell wall during thermal modification. The uniformity of ASE' for TM samples may then be explained by domination of the cross-linkage phenomenon. However, the ASE values reflect the macroscopic changes of the samples and in this case TM samples have lower ASE results than the best ELO treatments, *e.g.* EA7, SE2, A5 and A3B.

As expected, the AC samples showed the highest ASE results since a greater part of hydroxyl groups responsible for moisture adsorption has been substituted by anhydride. At the same time it is expected that the introduction of relatively bulky acetyl group into the wood cell wall results in significant cell wall damage.

From the results above it is concluded that treatment with ELO provides better results than thermal modification regarding the material dimensional stability. However, AC remains the best treatment to produce highly dimensionally stable material.

A logical relationship would be that the higher the positive ASE', the higher the ASE. However, this is not the case (*e.g.* AC treatment ASE and ASE' results). Other factors play a fundamental role and this analysis ensures only a limited insight of the occurrence.

The mean values of the ASE after each cycle for the treatments are presented in Table 12.

Table 12. Mean values of ASE (%) per cycle for each treatment

Treatment Code	Mean ASE [%] per cycle			
	1st	2nd	3rd	4th
SE1	34.6	37.7	38.9	38.0
SE2	46.4	49.9	51.8	51.2
Aad	40.0	40.0	40.7	39.8
A10	42.6	44.5	44.4	43.4
A7	43.2	45.3	46.2	46.0
A5	45.3	45.9	47.3	51.0
A3	46.1	47.6	48.4	50.0
A3B	46.2	49.4	50.6	51.6
EA7	49.5	54.1	55.9	56.6

It can be observed that for most of the treatments the ASE increased per cycle, however for SE1, SE2, Aad, A10 and A7 treatments the ASE slightly decreased from the cycles 3 to 4. Among all these treatments, the EA7 treatment provides the best results with an average ASE of 54. This can be explained by the fact that the wood was less degraded by the acid in this case since the samples were first impregnated with ELO which prevented hydrolysis of the carbohydrates.

3.3 Mechanical tests

Elasticity – MOE

The results of the modulus of elasticity tests are presented in Figure 12. More detailed results are collated in Appendix 4. The results from the one-way ANOVA test are presented in Table 13.

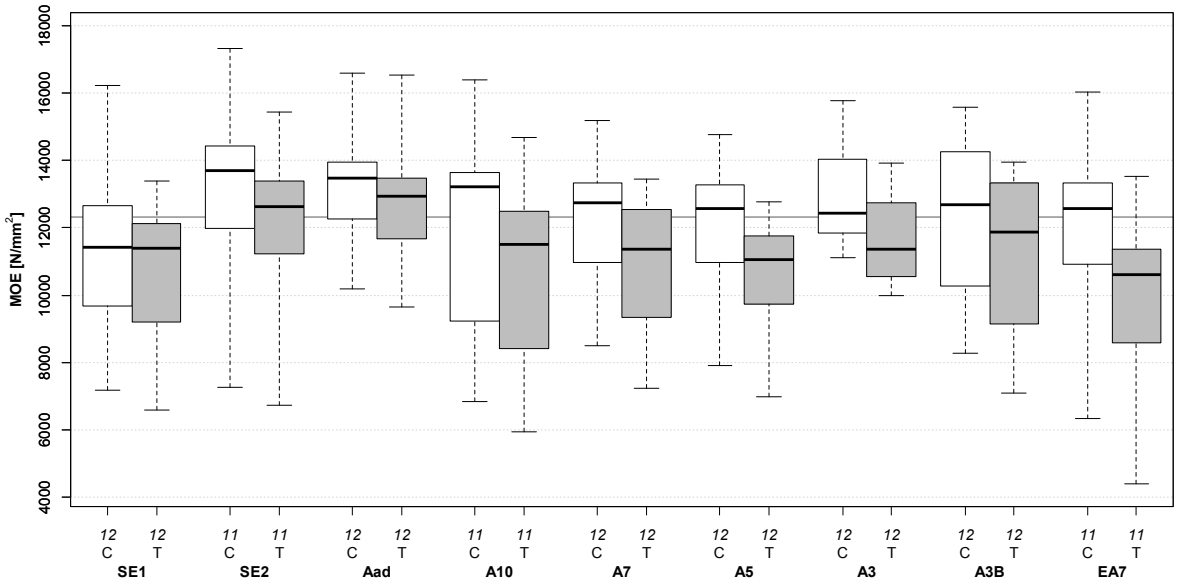

Figure 12. Modulus of elasticity (N/mm^2) for each treatment and for both the control samples (white boxes) and the corresponding treated samples (grey boxes). The values of MOE are shown on the y-axis; the x-axis shows the treatment code, the key letters C and T indicating control and treated samples, and the number of samples used. The horizontal black line (across the graph) represents the mean value of all control samples (of all treatments).

A trend of MOE decrease was observed for the treated samples. The control MOE values were similar to the results obtained in the work of Terziev and Panov (2011). However, the authors found an increase in MOE from the two ELO treatments performed, while the results above show a reverse effect.

Strength – MOR

The results of the modulus of rupture tests (ultimate bending strength) are presented in Figure 13. More detailed results are collated in Appendix 5. The results from the one-way ANOVA test are presented in Table 13.

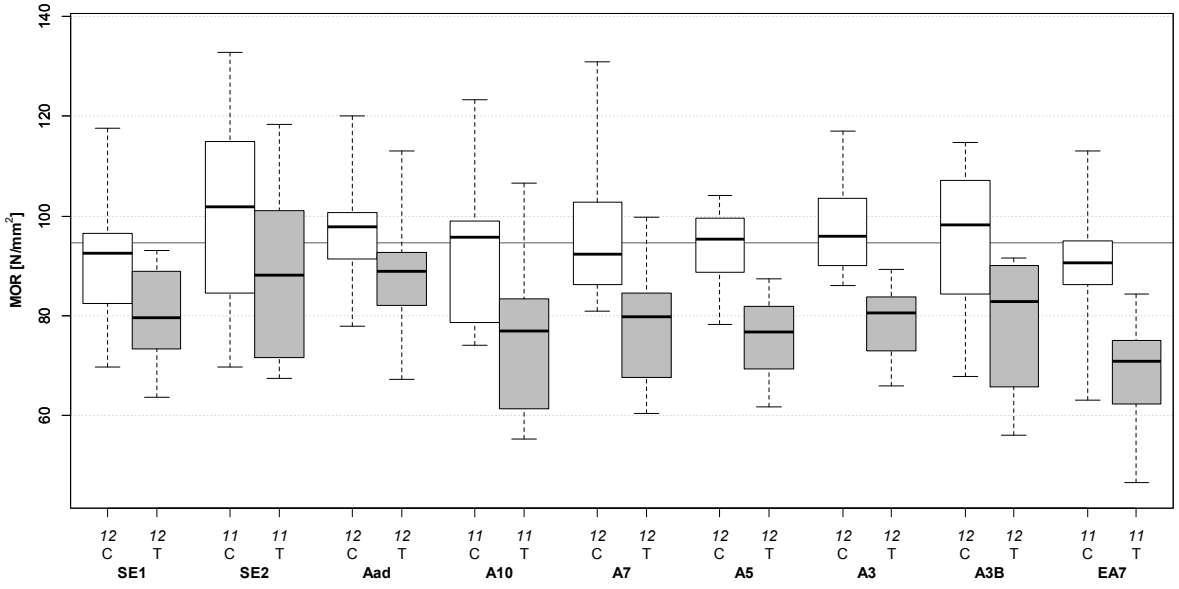

Figure 13. Modulus of rupture (N/mm^2) for each treatment and for both the control samples (white boxes) and corresponding treated samples (grey boxes). Explanations of Figure are as in Figure 12.

The MOR values of the untreated samples ranged from 89 to 100 N/mm^2, while the corresponding results for treated samples ranged from 68 to 88 N/mm2. Thus, ELO treatments resulted in an average of 16% loss in the strength. Basically, all samples subjected to AA impregnation in Steps 1 or 2 were expected to show a decrease in the strength because of the hydrolysis of carbohydrates. The extent of the decrease depends on the AA concentration, temperature, duration of exposure, whether the AA is impregnated in Step 1 or in Step 2 and the extent of recovery by ELO impregnation and polymerization. A significant decrease in MOR between control and treated samples was monitored after the A7, A5, A3 and EA7 treatments. A slightly lower decrease was measured for the Aad, A10 and A3B treatments. A smaller decrease in MOR was found for the SE1 treatment. The SE2 treatment gave only a slight decrease in the MOR.

The control MOR values are within the expected range; although the results obtained in the work of Terziev and Panov (2011) were slightly greater. However, a contradiction was found in this study. The authors found an increase in MOR after the ELO treatments performed, while these results show otherwise.

Hardness (Brinell) perpendicular to grain

The results of the hardness (Brinell) perpendicular to grain are presented in Figure 14. More detailed results are collated in Appendix 6. The results from the one-way ANOVA test are presented in Table 13.

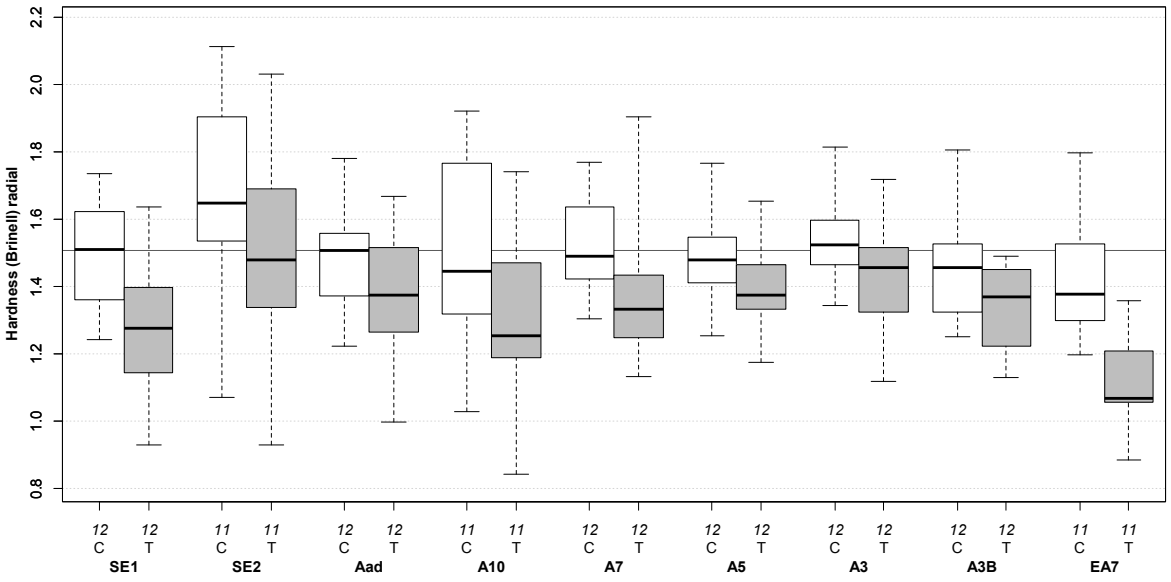

Figure 14. Hardness (Brinell) perpendicular to grain for each treatment and for both the control samples (white boxes) and the corresponding treated samples (grey boxes). Explanations of Figure are as in Figure 12.

As outlined above, insertion of bulky chemicals into the wood cell wall results in loss of mechanical performance. This process is known as plasticization. The hardness will then depend mainly on the oil uptake and the extent of polymerization of ELO. Indeed, the higher the uptake, the more stiff the material is but also a high polymerization degree will provide stiff material and vice versa. Thus, the low hardness value observed for the EA7 treatment samples is most likely due to the relatively high uptake obtained in this case compared to the other treatments.

The hardness determined in the work of Terziev & Panov (2011) was also perpendicular to the grain measured on the tangential surface, while in this study the determined hardness was

measured on the radial surface. Hence, a direct comparison of results is not possible, as the different results obtained for the control samples demonstrate. A decrease in the hardness was found in this study, while Terziev and Panov (2011) reported an increase.

Hardness (Brinell) parallel to grain

The results of the hardness (Brinell) parallel to grain are presented in Figure 15. More detailed results are collated in Appendix 7. The results from the one-way ANOVA test are presented in Table 13.

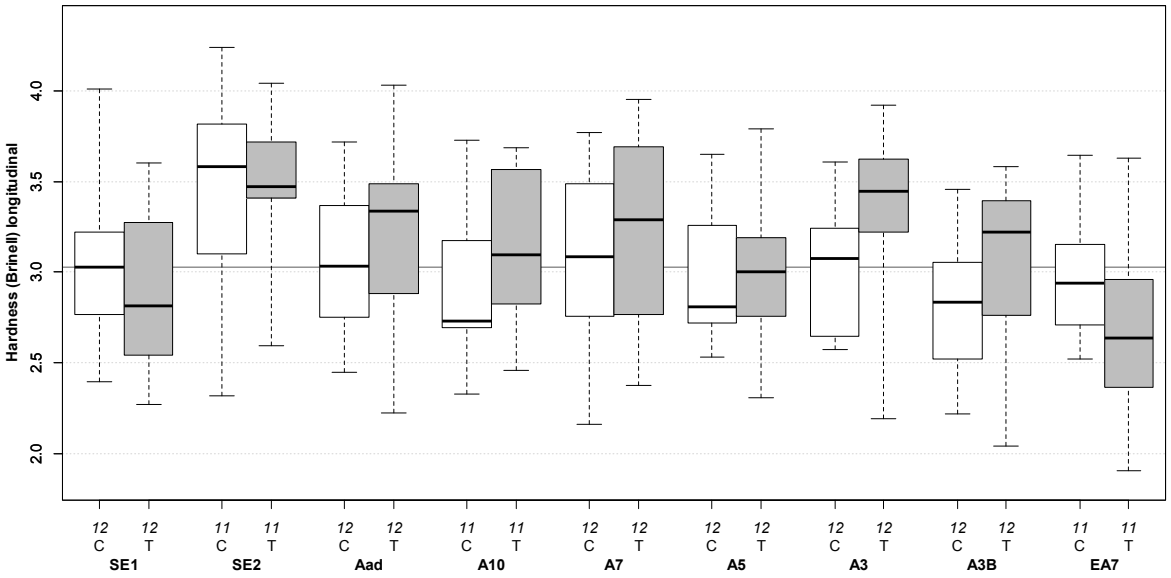

Figure 15. Hardness (Brinell) parallel to grain for each treatment and for both the control samples (white boxes) and the corresponding treated samples (grey boxes). Explanations of Figure are as in Figure 12.

The same argument as above is valid for hardness (Brinell) parallel to grain; even in this case the degree of polymerization of oil influenced the stiffness of the material. The values increased or decreased depending on the treatment. The hardness results showed a very clear upward trend for the A3 treatment. A somewhat lower increase was found as a result of the A10 and A3B treatments. For the SE1, SE2, Aad, A7 and A5 treatments no change in hardness could be detected. However, the EA7 treatment showed a slight decreasing trend.

Compression

The results of the compression (parallel to grain) are presented in Figure 16. More detailed results are collated in Appendix 8. The results from the one-way ANOVA test are presented in Table 13.

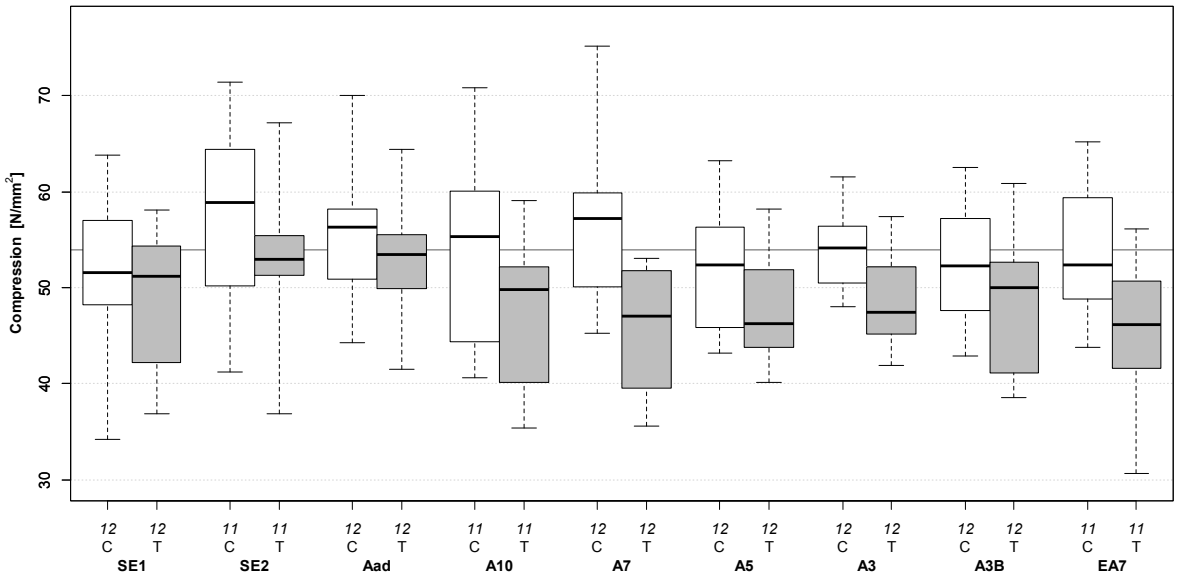

Figure 16. Compression (N/mm^2) for each treatment and for both the control samples (white boxes) and the corresponding treated samples (grey boxes). Explanations of Figure are as in Figure 12.

A tendency of decrease in compression strength can be monitored between the control and treated samples for almost all treatments. The A3 and A7 treatments showed a clear trend while A10, A5 and A3B treatments demonstrated only a weak trend. The other treatments did not show a difference between the control and treated samples.

The analysis of variance results (one-way ANOVA) per treatment for each of the measured mechanical properties are collated in Table 13. The results where *p* is smaller than 0.05 (*i.e.* the difference between the control and treated samples is statistically significant at 95% interval) have been highlighted by red bold style.

Table 13. Analysis of variance per treatment and measured property. The compared number of samples (control:treated, N:N) and the p-values for the properties MOE, MOR, hardness (Brinell) perpendicular to grain (HB ⊥), hardness (Brinell) perallel to grain (HB ∥), and compression are shown

Treatment		p-value				
Code	N:N	MOE	MOR	HB ⊥	HB ∥	Compression
SE1	12:12	0.510	**0.031**	**0.006**	0.344	0.326
SE2	11:11	0.415	0.177	0.209	0.872	0.303
Aad	12:12	0.549	0.051	0.116	0.355	0.372
A10	11:11	0.382	**0.022**	0.136	0.210	0.128
A7	12:12	0.112	**0.002**	**0.035**	0.515	**0.002**
A5	12:12	0.068	**0.000**	0.064	0.854	0.118
A3	12:12	**0.029**	**0.000**	0.135	0.070	**0.007**
A3B	12:12	0.271	**0.007**	0.077	0.222	0.096
EA7	11:11	0.106	**0.001**	**0.000**	0.184	**0.026**

** when $p < 0.05$, statistically significant difference exists between the control and treated samples*

The ANOVA analysis proved that there are certain treatments that introduced statistically significant changes of some mechanical properties of the treated wood.

According to the *p*-values in Table 13, the property where the treatments had the greatest effect was the MOR (significant difference in seven of the nine treatments), followed by

hardness (Brinell) perpendicular to grain and compression (in both cases determined for three of the nine treatments), next was the MOE (in only one treatment) and in hardness (Brinell) parallel to grain no significant difference at all for any treatment.

A summary of the results from all mechanical tests, in terms of change of each property in percentage is presented in Table 14. The changes of the properties were calculated by the percentage difference between the control and the modified samples. The values where a significant difference exists have been highlighted by red bold style.

Table 14. Retention and relative change of selected mechanical properties. The data show treatments, number of samples, mean retentions and the change (%) of the MOE, MOR, hardness (Brinell) perpendicular to grain (HB ⊥), hardness (Brinell) perallel to grain (HB ∥), and compression

Treatment code	N	Retention $_{T\text{-}B}$ [kg/m^3]	Change in [%]				
			MOE	MOR	HB ⊥	HB ∥	Compression
SE1	12	78	-5	**-11**	**-14**	-5	-5
SE2	11	107	-7	-11	-9	3	-7
Aad	12	90	-3	-9	-8	6	-4
A10	11	84	-10	**-19**	-11	9	-11
A7	12	87	-11	**-18**	**-10**	5	**-19**
A5	12	106	-12	**-18**	-7	2	-7
A3	12	101	**-10**	**-19**	-6	12	**-10**
A3B	12	72	-10	**-18**	-7	10	-9
EA7	11	144	-18	**-24**	**-21**	-9	**-15**

More detailed results for each property can be found in the Appendices 4-8.

According to the significance of the results proved by the *p*-values, it can be concluded that the ELO treatments resulted in decrease of the bending strength (MOR). The SE2 and Aad treatments did not show a statistically significant decrease in any of the measured properties.

The EA7 treatment ensured with statistical significance the largest decrease in MOR, HB perpendicular to grain and compression. Even though without statistical significance the box and whiskers plots also indicated a decrease for the MOE and HB parallel to grain. Furthermore, the EA7 treatment showed the highest overall decreases in the studied mechanical properties except for the compression strength.

The A7 treatment also showed a decrease in the same mechanical properties as the EA7 treatment. The A3 treatment shows a decrease in MOE, MOR and compression. Next follows the SE1 treatment showing a decrease in only two properties, MOR and HB perpendicular to the grain.

In the work of Terziev and Panov (2011), an increase of the mechanical properties MOE, MOR, impact bending strength and hardness of ELO treated Scots pine sapwood was reported. The authors used only 20 samples and retentions of about 100 and 200 kg/m^3. The study showed also a direct correlation between the retention and the increase of the MOE, MOR and hardness properties. The difference in the results of Terziev and Panov (2011) and these in the present study can be interpreted by the curing involved. The curing duration in this study was 14 or 20 days at elevated temperatures which probably drastically decreased the mechanical properties due to hydrolysis of the main wood structural compounds by the action of AA. In the study of Terziev and Panov (2011), curing was carried out for only 16 h; after

that the samples were stored at room climate for several months. The way the AA is introduced into the wood plays a very essential role. When mixed with ELO, the AA possesses less destructive properties because it is involved in the opening of the epoxy rings. This is confirmed by the treatment SE2 which is a copy of the technology applied by Terziev and Panov (2011); the obtained results show no significant decrease in any of the studied properties even after long-term curing!

The relationship between the retentions of ELO and the decrease of MOR was insignificant and confirmed by a low regression coefficient ($R^2 = 0.22$).

The ELO treatments where the AA was impregnated separately in Step 1 or in Step 2 seem to be the explanation for the decrease in MOR. The AA has damaged the wood polymeric constituents (most likely hemicelluloses, since these are the most susceptible to degradation). This damage did not influence neither the calculated angles α and β, nor the ASE'. The Aad with very low adsorbed AA did not show a statistical decrease in the mechanical properties.

The largest decrease in the mechanical properties of the EA7 treatment may be explained by the high oil uptake compared to the other treatments. Since the AA was impregnated in Step 2, it remained inside the wood structure damaging the wood polymeric constituents to a greater degree. However, it also should be remembered that the retention of AA in the EA7 treatment exceeded significantly with 50 to 80% the AA amount in the other trials, *i.e.* 337 kg/m^3 for samples A and 254 kg/m^3 for samples B.

3.4 Fourier transform infrared spectroscopy

The chemical changes of the ELO treated wood were analyzed by FT-IR spectroscopy. This technique is useful for examining chemical variations after the ELO treatment since it is able to determine the intensity of specific bonds and functional groups in polymers.

Figure 17 compares the FT-IR spectra recorded for the untreated and treated wood samples in the finger print region 4000-450 cm^{-1}. All spectra were normalized using the lignin characteristic band at 1505 cm^{-1} as a reference. The peaks that showed important alterations were 2928, 1738, 1373 and region 1300-1193 cm^{-1}; otherwise, the general character of the spectra remained unchanged. All these absorption bands increased significantly as intensity after modification with ELO. However, these results should be interpreted cautiously since the same bands in the same finger print were observed in the spectra of ELO (Figure 18). Nevertheless, these new bands could be attributed to new functional groups grafted to the wood namely, the carbonyl stretching vibration at 1738 cm^{-1} ($\nu_{C=O}$), the C-O stretching vibrations between 1193 and 1300 cm^{-1} (ν_{C-O}) and the methyl vibrations at 2928-2857 cm^{-1} (ν_{C-H}) and 1373 cm^{-1} (δ_{C-H}).

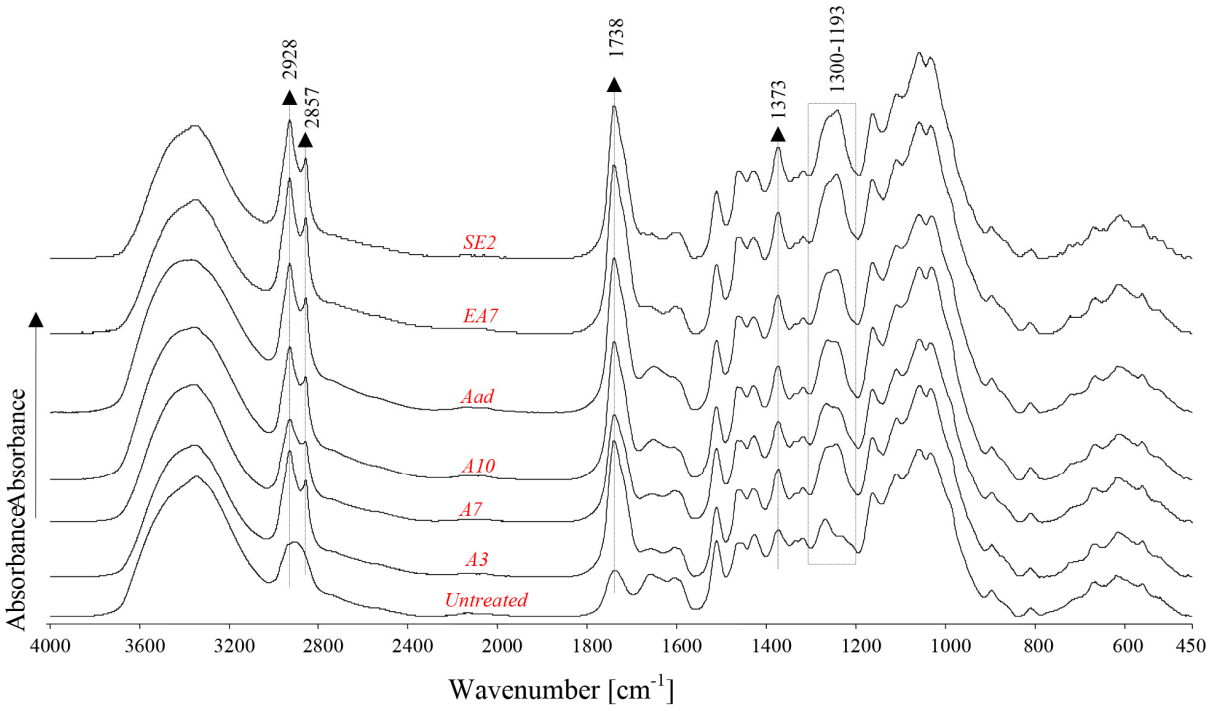

Figure 17. FT-IR spectra of untreated and modified wood with ELO for 6 of the studied treatments (in red).

Figure 18 compares the FT-IR spectra of ELO and polymerized ELO in the finger print region 4000-400 cm^{-1}.

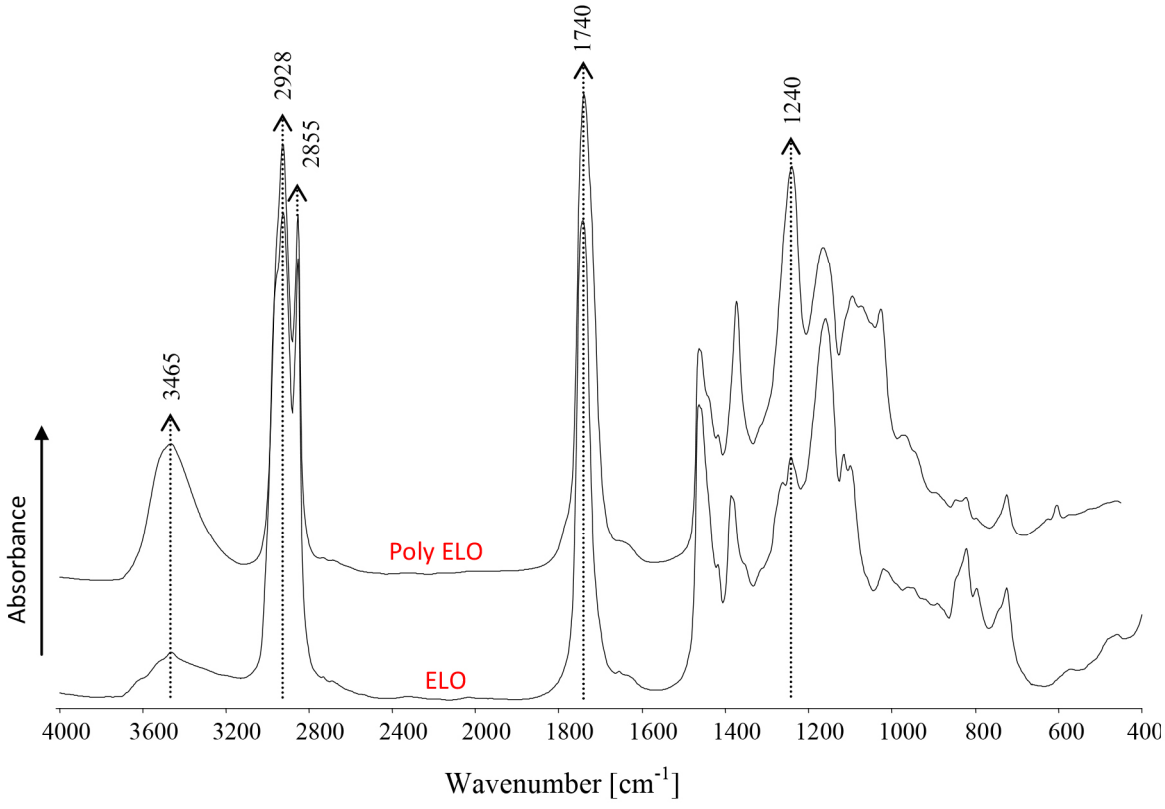

Figure 18. FT-IR spectra of the ELO and polymerized ELO.

4 Conclusions

The aim of the study was to investigate the use of a two-step process to impregnate epoxidised linseed oil in Scots pine sapwood and analyse the modified wood by means of its dimensional stability, hydrophobic and mechanical properties. Furthermore, FT-IR analysis was employed to evaluate the polymerization of ELO in the wood.

The results presented in this thesis demonstrated that the two-step process technology can achieve promising results. However, a feasible solution for practical application requires further studies to gain more knowledge about the mechanisms and effects of the treatments, and to select the most appropriate one. A clear drawback of the method seems to be a decrease of the modulus of rupture.

All studied treatments showed modification of the wood as indicated by the ASE values and suggested by the FT-IR analysis. The degree of modification probably differs between the studied trials but all of them *increase significantly the dimensional stability of the material*. This is shown by improved ASE for any treatment that varies between 38 to 56.6% (Table 12). In order to assess the achievement in the study it should be mentioned that the average measured ASE of the TM samples by ThermoWood technology was only 36.6% (Table 11), *i.e.* the proposed two-step treatments achieved better dimensional stability compared to that of the reference TM samples. The AC wood remains superior by its 80% ASE. In this way, the present work confirmed previous findings, *e.g.* Panov *et al.* 2010 and Ohmae *et al.* 2002 (regarding only the ASE of TM and AC wood).

According to the general theory (Hill 2006), the characters of the regression lines carry important information about the cell wall alterations caused by treatments and studied by WSOD cycles. When both water absorption and oven drying volumes *decrease* proportionally, this indicates loss of water soluble extractives and some fragments of the polysaccharides (single sugars or sugar oligomers) that have been produced by the action of the catalyst and temperature. At the same time there *is no loss of the modifying agent.* Examples of such treatments in Table 9 are SE2, A7, A5, A3, A3B and EA7. These treatments guarantee a reliable modification of the wood call wall and hence, high dimensional stability.
When the water absorption volumes *increase* while oven drying volumes decrease, this indicates *loss of the modifying agent* and, additionally, extractives and carbohydrates. Examples of such treatments in Table 9 are SE1 and Aad. These treatments are examples of less successful modification, *i.e.* less modifying agent in the wood cell wall and/or less bonds to the wood polymeric constituents. As a consequence a lower dimensional stability is achieved.

Leaching of modification agent is an inevitable process following any treatment. Depending on the amount of reagents and the way they were introduced into the wood structure, some treatments can be less economically viable, *e.g.* SE1 and A10 since they demonstrated about 25% leached formulation after only one WSOD cycle (Figure 9). In contrast to the above, EA7 had only 7% leached formulation. Leaching decreases with the cycles; it seems that after 2 cycles it comes to a constant level of approximately 1% per cycle.

The fact that a sufficient modification of wood always influences negatively some of the material mechanical properties was confirmed in the present study. The improvement of the dimensional stability was inversely related to measured modulus of rupture which was the most affected mechanical feature (Table 14) with a decrease of approximately 20%. At the

same time, no changes were found in the modulus of elasticity and hardness. The long duration of curing may explain the recorded changes, a fact that emphasizes the importance of the post-impregnation processing of modified wood.

The study recommends some of the trials for further industrial scale tests. For example, Aad *is the cheapest option* since the AA is introduced into wood by adsorption and a reasonable ASE of 39.8% is achieved while the mechanical properties are unchanged. When higher ASE is demanded, the A5, A3, A3B and EA7 treatments are recommended. All of them raise the ASE to more than 50% but decrease the modulus of rupture. The AA used in the former three treatments is diluted, *i.e.* cheap and less harmful for the equipment and personal. Some further optimization is needed consisting of less impregnated AA in trial EA7; this may improve the mechanical properties. Since the ELO modification ensures better dimensional stability of the material than TM, treated timber can be used in similar applications, *e.g.* paneling, decking, garden furniture, but even flooring are items of interest.

4.1 Suggestions for future work

Possibly a key aspect to consider which method, whether first catalyst or ELO impregnation, will be the best practical solution, would be to evaluate which method makes possible better control of the changes of wood properties.

Possibly a treatment using AA introduced by the adsorption approach with short treatment time and increasing adsorption speed may decrease the damage to wood polymeric constituents. A suggestion may be to carry out the following: 1) drying of timber to low MC; 2) immediately subject the timber to AA adsorption process for some hours under pressure; 3) apply ELO impregnation; 4) short curing at elevated temperature; 5) conditioning.

The EA7 trial suggests that another catalyst, acting much faster than AA, could be used. For instance, formic acid catalyses the epoxidation reaction faster since it is stronger acid than the AA. Naturally, this hypothesis should be tested in a laboratory prior to further implementation.

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Appendices

Appendix 1. Impregnation parameters

Tables with the operations and parameters (pressure, temperature and time) used in the impregnation procedure for the treatments.

ELO and AA mixture impregnation

Table 14. ELO and AA mixture impregnation operations followed and parameters used. This procedure was followed with both standard treatments, SE1 and SE2

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO & AA mixture	-	70	20
Pre-pressure to samples	1.25	-	20
Transfer ELO & AA mixture to cylinder with samples	*NA*	*NA*	*NA*
Pressure	4	70	60
Pressure release	-	80	60
Extraction of ELO & AA mixture	*NA*	*NA*	*NA*
Vacuum	vacuum	-	20
Extraction of leached ELO & AA mixture	*NA*	*NA*	*NA*
Pre-curing with pressure and remaining heat	5	-	60

AA adsorption and ELO impregnation (Aad)

Table 15. ELO impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO	-	70	40
Pre-pressure to samples	1.25	70*	20
Transfer ELO to cylinder with samples	*NA*	*NA*	*NA*
Pressure	3.75	70	50
Pressure release	-	80	50
Extraction of ELO	*NA*	*NA*	*NA*
Vacuum	vacuum	-	20
Extraction of leached ELO	*NA*	*NA*	*NA*
Pre-curing with pressure and remaining heat	5	70*	120*

AA impregnation at 100% C and ELO impregnation (A10)

Table 16. AA impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-pressure to samples	5	-	10
Transfer AA to cylinder with samples	*NA*	*NA*	*NA*
Pressure	6	-	20*
Extraction of AA	*NA*	*NA*	*NA*
Vacuum	Non*	-	-
Extraction of leached AA	*NA*	*NA*	*NA*

Table 17. ELO impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO	-	70	40
Pre-pressure to samples	1.25	70*	20
Transfer ELO to cylinder with samples	*NA*	*NA*	*NA*
Pressure	3.75	70	50*
Pressure release	-	80	50*
Extraction of ELO	*NA*	*NA*	*NA*
Vacuum	vacuum	-	20
Extraction of leached ELO	*NA*	*NA*	*NA*
Pre-curing with pressure and remaining heat	5	70*	120*

AA impregnation at 70% C and ELO impregnation (A7)

Table 18. AA impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-pressure to samples	5	-	10
Transfer AA to cylinder with samples	*NA*	*NA*	*NA*
Pressure	6	-	20*
Extraction of AA	*NA*	*NA*	*NA*
Vacuum	vacuum	-	10*
Extraction of leached AA	*NA*	*NA*	*NA*

Table 19. ELO impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO	-	70	40
Pre-pressure to samples	1.25	50*	20
Transfer ELO to cylinder with samples	*NA*	*NA*	*NA*
Pressure	3.75	70	60*
Pressure release	-	80	50*
Extraction of ELO	*NA*	*NA*	*NA*
Vacuum	vacuum	-	20
Extraction of leached ELO	*NA*	*NA*	*NA*
Pre-curing with pressure and remaining heat	5	70*	120*

AA impregnation at 50% C and ELO impregnation (A5)

Table 20. AA impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-pressure to samples	5	-	10
Transfer AA to cylinder with samples	*NA*	*NA*	*NA*
Pressure	6	-	25*
Extraction of AA	*NA*	*NA*	*NA*
Vacuum	vacuum	-	10*
Extraction of leached AA	*NA*	*NA*	*NA*

Table 21. ELO impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO	-	70	40
Pre-pressure to samples	1.25	-	20
Transfer ELO to cylinder with samples	*NA*	*NA*	*NA*
Pressure	3.75	70	60*
Pressure release	-	80	50*
Extraction of ELO	*NA*	*NA*	*NA*
Vacuum	vacuum	-	20
Extraction of leached ELO	*NA*	*NA*	*NA*
Pre-curing with pressure and remaining heat	5	-*	60*

AA impregnation at 30% C and ELO impregnation (A3)

Table 22. AA impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-pressure to samples	5	-	10
Transfer AA to cylinder with samples	*NA*	*NA*	*NA*
Pressure	6	-	25*
Extraction of AA	*NA*	*NA*	*NA*
Vacuum	vacuum	-	10
Extraction of leached AA	*NA*	*NA*	*NA*

Table 23. ELO impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO	-	70	40
Pre-pressure to samples	1.25	-*	20
Transfer ELO to cylinder with samples	*NA*	*NA*	*NA*
Pressure	3.75	70	60*
Pressure release	-	80	60*
Extraction of ELO	*NA*	*NA*	*NA*
Vacuum	vacuum	-	20
Extraction of leached ELO	*NA*	*NA*	*NA*
Pre-curing with pressure and remaining heat	5	-*	60*

AA impregnation at 30% C with BA and ELO impregnation (A3B)

Table 24. AA impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-pressure to samples	5	-	10
Transfer AA to cylinder with samples	*NA*	*NA*	*NA*
Pressure	6	-	25*
Extraction of AA	*NA*	*NA*	*NA*
Vacuum	vacuum	-	10*
Extraction of leached AA	*NA*	*NA*	*NA*

Table 25. ELO impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO	-	70	40
Pre-pressure to samples	1.25	-	20
Transfer ELO to cylinder with samples	*NA*	*NA*	*NA*
Pressure	3.75	70	60*
Pressure release	-	80	60*
Extraction of ELO	*NA*	*NA*	*NA*
Vacuum	vacuum	-	20
Extraction of leached ELO	*NA*	*NA*	*NA*
Pre-curing with pressure and remaining heat	5	-*	60*

ELO impregnation and AA impregnation at 70% C (EA7)

Table 26. ELO impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO	-	70	40
Pre-pressure to samples	1.25	-	20
Transfer ELO to cylinder with samples	*NA*	*NA*	*NA*
Pressure	3.75	70	60*
Pressure release	-	80	60*
Extraction of ELO	*NA*	*NA*	*NA*
Vacuum	vacuum	-	20
Extraction of leached ELO	*NA*	*NA*	*NA*

Table 27. AA impregnation operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-pressure to samples	5	-	10
Transfer AA to cylinder with samples	*NA*	*NA*	*NA*
Pressure	6	-	25*
Extraction of AA	*NA*	*NA*	*NA*
Vacuum	vacuum	-	10*
Extraction of leached ELO & AA mixture	*NA*	*NA*	*NA*

Table 28. ELO pre-curing operations followed and parameters used

Operation	Pressure	Temperature	Time
	[bar]	[ºC]	[min]
Pre-heating ELO	-	70	40
Transfer ELO to cylinder with samples	*NA*	*NA*	*NA*
Pre-curing with pressure and remaining heat	*5*	-*	*60*

Appendix 2. Treatment retention results

Tables 29 and *30* show more detailed figures of the complete treatment retention results for samples A and B for each treatment.

Table 29. Retention after complete treatment of samples A

Treatment		Retention $_T$ [kg/m^3]			
Code	**N**	**Mean**	**Min**	**Max**	**SD**
SE1	13	92	69	118	15
SE2	12	148	123	169	14
Aad	13	116	94	131	13
A10	11	59	43	75	9
A7	13	106	67	162	28
A5	13	187	157	228	21
A3	6	170	150	179	10
A3B	11	172	96	198	27
EA7	10	222	157	277	40

Table 30. Retention after complete treatment of samples B

Treatment		Retention $_T$ [kg/m^3]			
Code	**N**	**Mean**	**Min**	**Max**	**SD**
SE1	12	78	67	90	69
SE2	11	107	85	126	16
Aad	12	90	58	107	14
A10	11	84	63	113	14
A7	12	87	49	146	28
A5	12	106	73	135	21
A3	12	101	67	144	23
A3B	12	72	59	101	14
EA7	11	144	117	188	21

Appendix 3. Volume-cycles figures results

Volume-cycles figures for each of the treatments not presented previously.

SE1

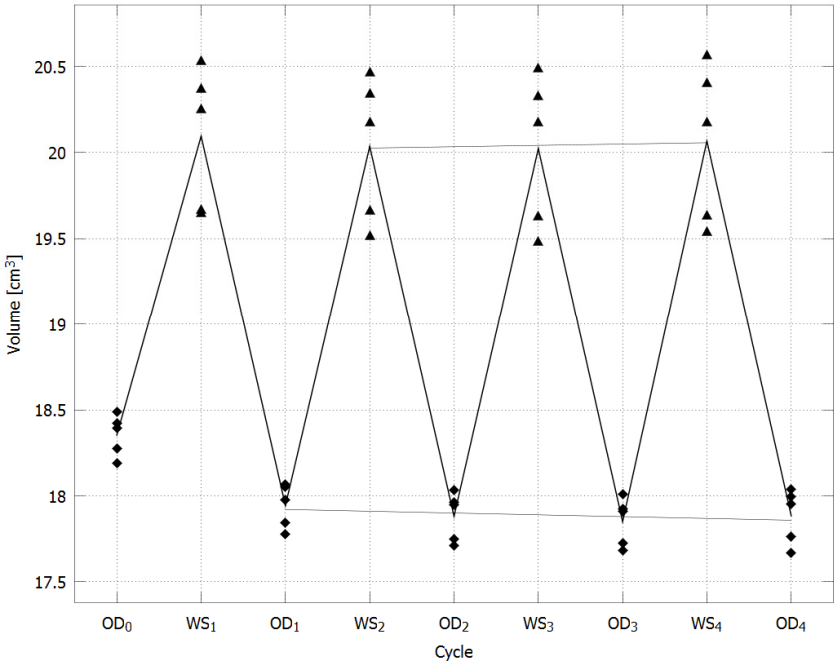

Figure 19. Water absorption-oven drying cycles for SE1 treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). OD and WS states are represented by diamond- and triangle-shaped markers respectively. The line going from the mean volume value of the first state to the mean volume value of next one until the last state represents the path followed by the samples during the series of cycles. The regression line fitting the data from the states OD_1, OD_2, OD_3 and OD_4 represents the change in volume of the samples at the OD state. The regression line fitting the data from the states WS_2, WS_3 and WS_4 represents the change in volume of the samples at the WS state.

Aad

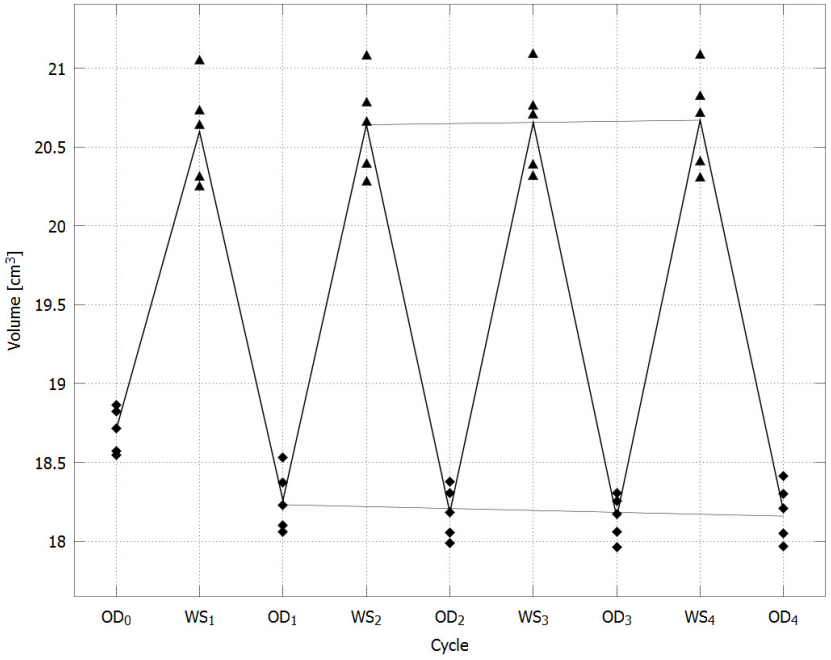

Figure 20. Water absorption-oven drying cycles for Aad treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). Explanations of Figure are as in Figure 19.

A10

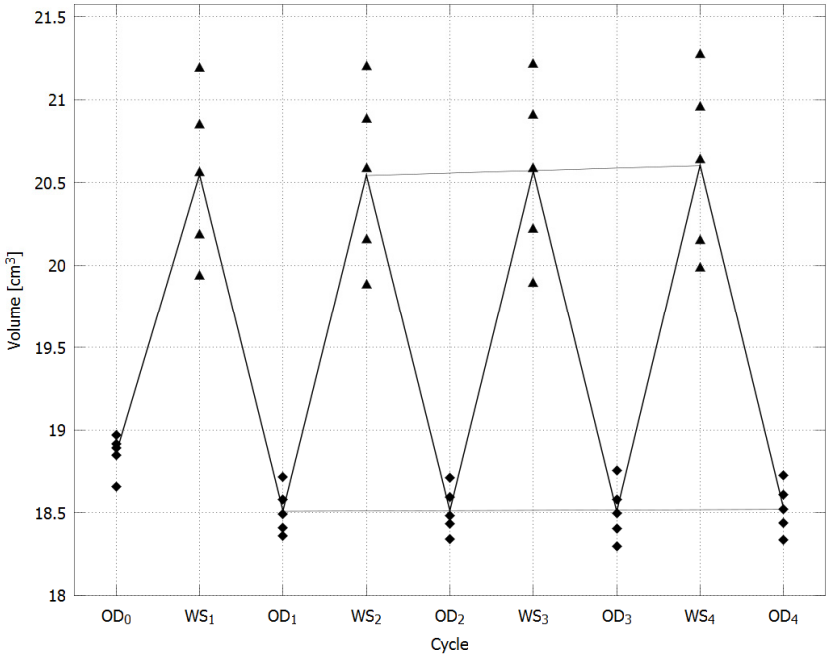

Figure 21. Water absorption-oven drying cycles for A10 treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). Explanations of Figure are as in Figure 19.

A7

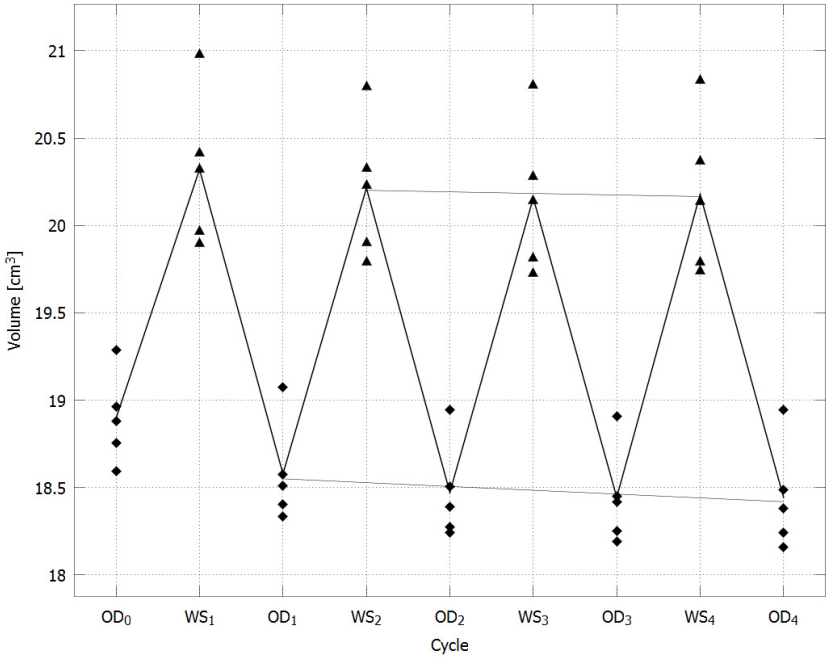

Figure 22. Water absorption-oven drying cycles for A7 treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). Explanations of Figure are as in Figure 19.

A5

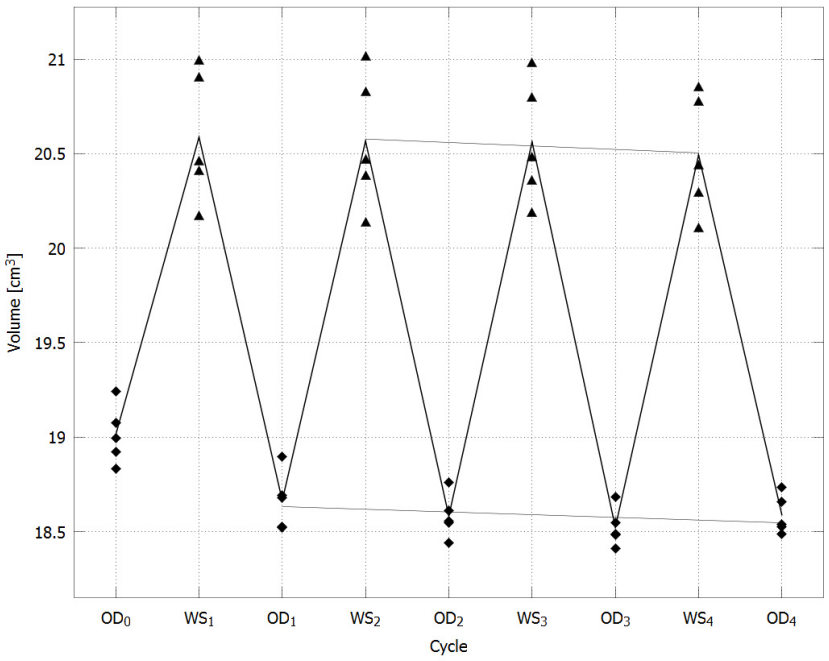

Figure 23. Water absorption-oven drying cycles for A5 treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). Explanations of Figure are as in Figure 19.

A3

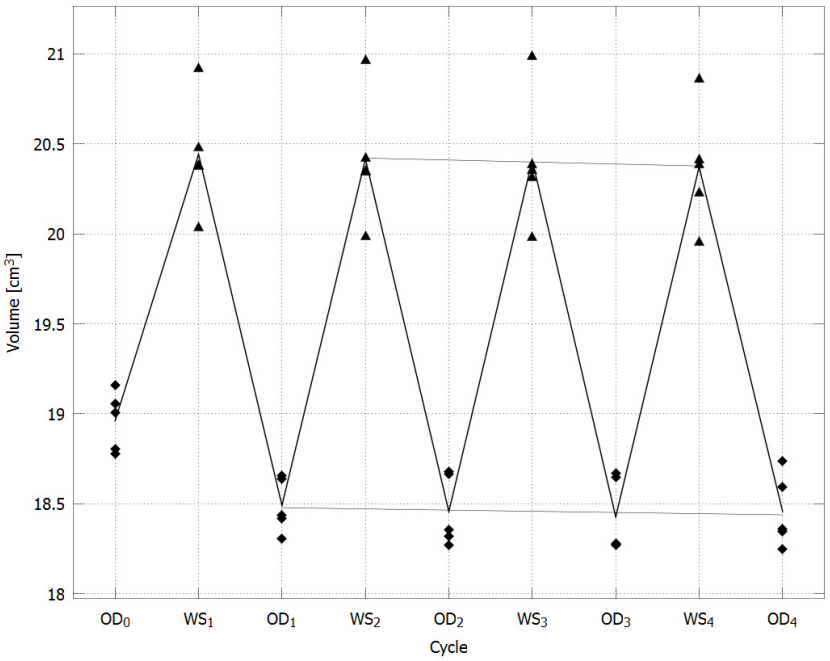

Figure 24. Water absorption-oven drying cycles for A3 treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). Explanations of Figure are as in Figure 19.

A3B

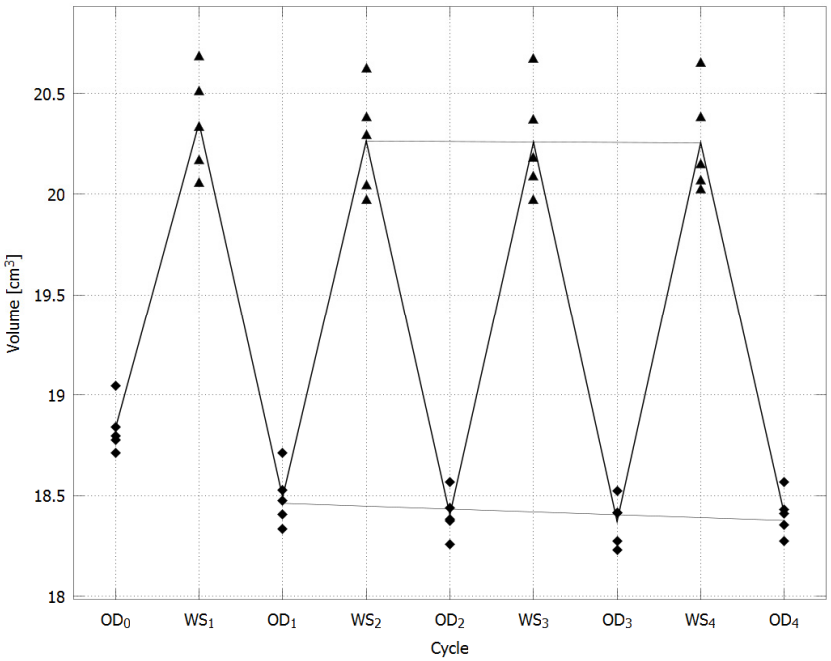

Figure 25. Water absorption-oven drying cycles for A3B treated samples, the volume (cm^3) at each state, for the start point (sub-index 0) and all cycles (sub-indexes 1 to 4). Explanations of Figure are as in Figure 19.

Appendix 4. MOE results

Table 31 shows more detailed results.

Table 31. MOE results for each treatment

Treatment Code	Samples		MOE		Change in MOE	
	Type	N	Mean [N/mm^2]	SD [N/mm^2]	Mean [%]	SD [%]
SE1	Control	12	11405	2304	-5	7
	Treated	12	10822	1942		
SE2	Control	11	13036	2806	-7	3
	Treated	11	12085	2551		
Aad	Control	12	13181	1750	-3	7
	Treated	12	12757	1664		
A10	Control	11	11963	3384	-10	4
	Treated	11	10739	3025		
A7	Control	12	12287	1897	-11	5
	Treated	12	11003	1900		
A5	Control	12	12070	1907	-12	3
	Treated	12	10649	1717		
A3	Control	12	12951	1475	-10	5
	Treated	12	11619	1316		
A3B	Control	12	12306	2525	-10	7
	Treated	12	11148	2501		
EA7	Control	11	11755	2829	-18	6
	Treated	11	9743	2746		

Appendix 5. MOR results

Table 32 shows more detailed results.

Table 32. MOR results for each treatment

Treatment Code	Samples		MOR		Change in MOR	
	Type	N	Mean [N/mm^2]	SD [N/mm^2]	Mean [%]	SD [%]
SE1	Control	12	91	12	-11	6
	Treated	12	80	10		
SE2	Control	11	100	21	-11	6
	Treated	11	89	18		
Aad	Control	12	97	11	-9	7
	Treated	12	88	11		
A10	Control	11	93	16	-19	5
	Treated	11	76	16		
A7	Control	12	96	14	-18	7
	Treated	12	78	11		
A5	Control	12	93	8	-18	4
	Treated	12	76	8		
A3	Control	12	98	10	-19	6
	Treated	12	79	7		
A3B	Control	12	95	15	-18	5
	Treated	12	78	13		
EA7	Control	11	89	13	-24	4
	Treated	11	68	11		

Appendix 6. Hardness (Brinell) - perpendicular results

Table 33 shows more detailed results.

Table 33. Hardness (Brinell) perpendicular to grain results for each treatment

Treatment	Samples		HB ⊥		Change in HB ⊥	
					Mean	SD
Code	Type	N	Mean	SD	[%]	[%]
SE1	Control	12	1.49	0.16	-14	10
	Treated	12	1.28	0.18		
SE2	Control	11	1.67	0.31	-9	18
	Treated	11	1.50	0.30		
Aad	Control	12	1.49	0.15	-8	10
	Treated	12	1.37	0.19		
A10	Control	11	1.50	0.30	-11	15
	Treated	11	1.32	0.25		
A7	Control	12	1.53	0.15	-10	11
	Treated	12	1.37	0.20		
A5	Control	12	1.50	0.15	-7	9
	Treated	12	1.39	0.13		
A3	Control	12	1.53	0.13	-6	10
	Treated	12	1.44	0.16		
A3B	Control	12	1.45	0.15	-7	7
	Treated	12	1.34	0.13		
EA7	Control	11	1.42	0.18	-21	10
	Treated	11	1.11	0.14		

Appendix 7. Hardness (Brinell) - parallel results

Table 34 shows more detailed results.

Table 34. Hardness (Brinell) parallel to grain results for each treatment

Treatment	Samples		HB ∥		Change in HB ∥	
					Mean	SD
Code	Type	N	Mean	SD	[%]	[%]
SE1	Control	12	3.05	0.43	-5	15
	Treated	12	2.88	0.46		
SE2	Control	11	3.46	0.60	3	17
	Treated	11	3.50	0.40		
Aad	Control	12	3.06	0.39	6	15
	Treated	12	3.23	0.52		
A10	Control	11	2.91	0.41	9	16
	Treated	11	3.16	0.47		
A7	Control	12	3.10	0.49	5	14
	Treated	12	3.23	0.52		
A5	Control	12	2.97	0.38	2	17
	Treated	12	3.00	0.42		
A3	Control	12	3.01	0.36	12	18
	Treated	12	3.34	0.48		
A3B	Control	12	2.79	0.37	10	23
	Treated	12	3.02	0.53		
EA7	Control	11	2.95	0.34	-9	17
	Treated	11	2.69	0.53		

Appendix 8. Compression results

Table 35 shows more detailed results.

Table 35. Compression results for each treatment

Treatment Code	Samples		Compression		Change in Compression	
	Type	N	Mean [N/mm^2]	SD [N/mm^2]	Mean [%]	SD [%]
SE1	Control	12	51.9	8.2	-5	10
	Treated	12	48.8	7.0		
SE2	Control	11	56.9	10.0	-7	8
	Treated	11	52.8	8.4		
Aad	Control	12	55.0	7.0	-4	4
	Treated	12	52.6	6.0		
A10	Control	11	53.5	9.8	-11	5
	Treated	11	47.5	8.0		
A7	Control	12	56.7	8.1	-19	6
	Treated	12	45.8	6.4		
A5	Control	12	51.8	6.6	-7	9
	Treated	12	47.7	5.5		
A3	Control	12	54.2	4.5	-10	10
	Treated	12	48.5	4.9		
A3B	Control	12	52.5	6.4	-9	7
	Treated	12	47.7	7.1		
EA7	Control	11	53.6	7.6	-15	6
	Treated	11	45.8	7.6		

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